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Supplemental Information

Cascade CO_2 electroreduction enables efficient carbonate-free production of ethylene

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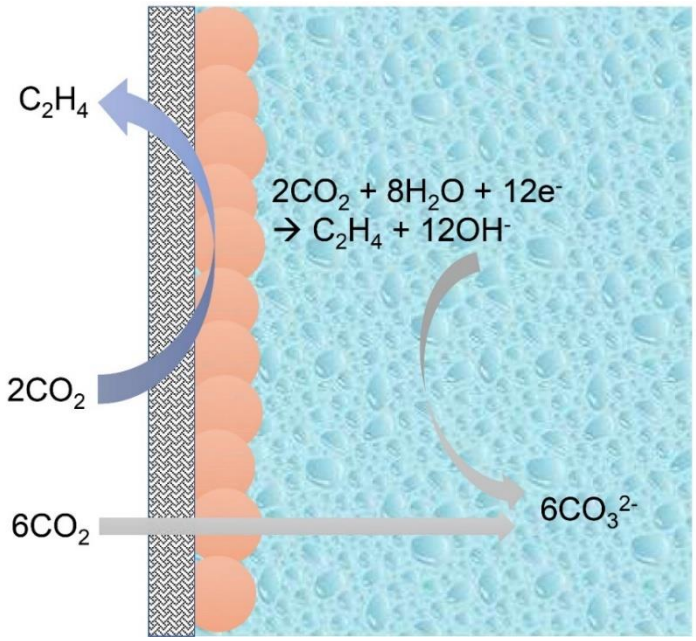


Figure S1. Mechanism of carbonate formation during CO_2 electroreduction. Producing 1 mole of C_2H_4 by CO_2RR generates 12 moles of OH^- which reacts with another 6 mole CO_2. If the C_2H_4 FE is 100%, the CO_2-to-C_2H_4 single-pass conversion is limited to 25%. Today's highest C_2H_4 FE remains below 80%. The maximum single-pass conversion would therefore be less than 20%.

Note S1. Selection of CO_2RR systems compared in techno-economic assessment. To assess the energy and cost associated with CO_2 reactant loss to carbonate, we performed energy and techno-economic assessments (TEA) for literature benchmark neutral and alkaline CO_2RR systems. We have compared the energy and cost distributions of producing ethylene for the SOEC:MEA system relying on cascade CO_2-to-CO and CO-to-C_2H_4 conversion steps with those for the reference CO_2RR system relying on direct route (CO_2-to-C_2H_4). As the reference systems based on direct route (CO_2-to-C_2H_4), we have considered two types: the neutral membrane electrode assembly (MEA) electrolyser[1] (labelled as "CO_2RR MEA" in Figure 1) and the alkaline flow cell electrolyser[2] (labelled as "CO_2RR alkaline flow cell" in Figure 1). These neutral and alkaline electrolysers are included in the light of their high performance metrics – high reaction rates (>100 mA cm^{-2}), high CO_2-to-C_2H_4 selectivity (>60%), and high full-cell energy efficiency (>20%). Other systems such as neutral flow cell electrolysers and H-cells were excluded from our techno-economic analysis, as they have not provided high current density or stability.

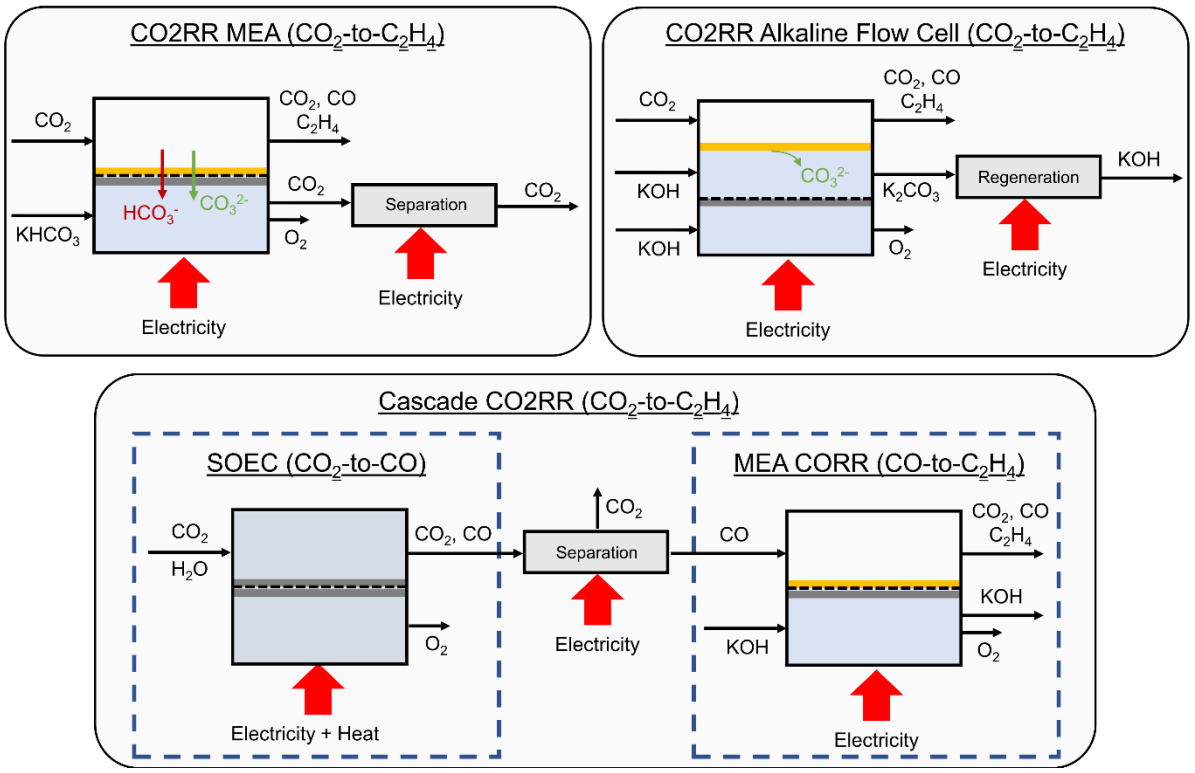


Figure S2. Block diagrams of CO_2RR MEA, CO_2RR alkaline flow cell, and Cascade CO_2RR.

Note S2. Techno-economic assessment. This section describes the TEA model used for all cost calculations. Here, we will walk through the details of calculating the cost of producing CO in a SOEC. All other electrolyser systems use the same base model outlined here, but inputs vary between each setup and these differences are highlighted.

In our model, we calculate the cost of producing 1 tonne of CO per day and use this as an input cost for our CORR calculations. Since 2 tonnes of CO are required per tonne of C_2H_4, a CO-producing plant would have to have double the output of our current model (2 tonnes CO per day) in order to meet the requirements for the C_2H_4 plant (1 tonne per day). By modelling this scenario in our TEA, we find that the production of C_2H_4 would be cheaper because the cost of CO per tonne decreases with the size of the plant. The only cost consideration in our model that does not scale linearly is the pressure-swing adsorption (PSA) module in our cathode separation. The capital cost for this component scales as the total cathode flow rate to the power of 0.7. Since this cost grows slower than a linear scaling, as we double our CO production rate, the cost of separation per tonne will decrease. Because the cost effects of plant scaling were outside the scope of the TEA in this work, we kept the production rate at 1 tonne per day for all chemicals and used the more conservative cost of CO.

The amount of electrolyte required in our TEA model was calculated using the ratio of 100 L electrolyte per m^2 of electrolyser. This ratio is based on approximate ratios used in lab-scale experiments and it provides a starting point to estimate electrolyte costs. Once a total volume of electrolyte is calculated, it is assumed to be circulated through the electrolyser constantly for one year before being completely replaced. Therefore, the total cost of purchasing electrolyte with a 100 L/m^2 ratio is reduced to a daily cost to find the cost per tonne of product. This calculation provides an estimate of the cost of electrolyte. In future, such costs estimates will benefit from operational data from larger scale deployments.

For the CORR:GOR demonstration, we did not consider the cost of glucose input to the anode side, or the value of the anode-side products. The net value of the anode-side products is higher than the glucose input, but would in practice require separation and associated cost. We focus here on ethylene as the sole product and note the potential for a glucose anode-side reaction to lower the cost of ethylene production.

The general model calculates the cost of producing 1 tonne of product (CO for the case of SOEC) in a plant with a production rate of 1 tonne per day, starting from CO_2. It is assumed that the only by-product produced on the cathode side is hydrogen and that the anode performs OER, producing only oxygen. Once the total amount of electrolyser materials, input chemicals, and electricity are purchased, there are some external systems that are modelled. At the cathode output, a PSA gas separation module is modelled to separate product from hydrogen and unreacted CO_2 so that the product can be sold, and the CO_2 can be recycled back into the electrolyser input. Similarly, a PSA gas separation module is modelled at the anode output to separate O_2 from any CO_2 that crosses through the membrane and bubbles out of the electrolyte. Once again, the CO_2 recovered from this separation can be recycled back to the electrolyser input. For alkaline systems, there will be a lot of CO_2 lost to carbonate in the KOH electrolyte. In order to recover this CO_2 and electrolyte, a regenerative calcium cycle is used. Finally, for the SOEC, which must be run at high temperature, the costs required to heat the electrolyser materials and chemical inputs as well as amine CO_2 scavenging are calculated. All these aspects are combined into a final cost or energy loss per tonne of product.

SOEC Input Parameters

For costs of CO produced in SOEC for the base case, the following input parameters were used. These values will be used for the sample calculation shown here:

Parameters	**Value**
CO_2 Cost (\$ tonne^{-1})	30
Electricity cost (\$ kWh^{-1})	0.03
Electrolyser cost (\$/kW^{-1})	250
Balance of plant (%)	50
Lang factor	1
Capacity factor	0.9

Cell voltage (V)	1.3
Faradaic efficiency (%)	100
Current density (mA cm^{-2})	800
Single pass conversion (%)	40
CO_2 crossover factor	0
System lifetime (year)	30
Catalyst/membrane lifetime (year)	5
Operation Temperature (°C)	800
Discount Rate (%)	5

Input CO_2

First, we find the amount of CO_2 required to produce 1 tonne of CO with 100% efficiency. All losses of CO_2 will be accounted for in other calculations that recycle CO_2 so that no new CO_2 is needed to be purchased. Also, even though the FE towards ethylene is sometimes less than 100%, we assume the only other product is H_2. (Since H_2 is formed from H_2O, not CO_2, we do not need to buy more CO_2 to account for this.)

The calculation is given by:

$$CO_2\ required\ \left[\frac{tonne\ CO_2}{tonne\ CO}\right] = CO\ output\ \left[tonne\frac{CO}{day}\right] \times \frac{molecular\ weight_{CO2}\left[\frac{g}{mol}\right]}{molecular\ weight_{CO}\left[\frac{g}{mol}\right]} \times molar\ ratio\ \left[\frac{CO_2}{CO}\right] \quad (1a)$$

Plugging in numbers gives us:

$$CO_2\ required\left[\frac{tonne\ CO_2}{tonne\ CO}\right] = 1\ tonne\frac{CO}{day} \times \frac{44\frac{g}{mol}}{28\frac{g}{mol}} \times 1 = 1.5714\ \frac{tonne\ CO_2}{tonne\ CO} \quad (1b)$$

Now we can multiply this number by the market price of CO_2 to find the cost component for our TEA. A 2015 CO_2 price forecast used 25 \$/short ton (1 short ton = 907.18 kg) as their 'high case' cost.[3] This gives a metric price of ~ 28 \$/tonne and after rounding, we achieve the price used in this work, 30 \$/tonne. The final cost of CO_2 per tonne of ethylene in our model is:

$$Cost\ of\ input\ CO_2\left[\frac{\$}{tonne\ CO}\right] = 30\ \frac{\$}{tonne\ CO_2} \times 1.5714\frac{tonne\ CO_2}{tonne\ CO} = \mathbf{47.14}\ \frac{\$}{\boldsymbol{tonne}\ \mathbf{CO}} \quad (2)$$

Electrolyser cost

The electrolyser cost for an SOEC is based on a cost estimate of ~ 250 \$ kW^{-1} for 25 kW solid oxide fuel cell water electrolysers (SOFCs) when 50 000 units are purchased.[4] These SOFCs had a performance objective of 400 mA cm^{-2} which was used as a reference current density during cost calculations.[4] To find the cost of the electrolyser, the total power needed was multiplied by the cost per kW provided above. Next, this cost was scaled by the input current density and reference current density (see below) in order to consider the area of electrolyser required. (If the current density is halved, double the amount of electrolyser material is needed.)

First, we find the moles of product formed per second in order to produce 1 tonne CO per day.

$$CO\ production\ \left[\frac{mol}{s}\right] = \frac{CO\ production\left[\frac{g}{day}\right]}{molecular\ weight_{CO}\left[\frac{g}{mol}\right] \times 86400\left[\frac{s}{day}\right]} \tag{3a}$$

$$CO\ production\ \left[\frac{mol}{s}\right] = \frac{1 \times \frac{10^6 g}{day}}{\frac{28g}{mol} \times \frac{86400s}{day}} = 0.41336\frac{mol}{s} \tag{3b}$$

Next, we can find the total current needed to produce this much CO, taking into account the loss of electrons if the FE is below 100%. (In the case of our SOEC, we assumed FE was 100%.)

$$Total\ current\ needed\ [A] = \frac{CO\ production\left[\frac{mol}{s}\right] \times electrons\ transferred \times Faraday's\ Constant}{FE[decimal]} \tag{4a}$$

Plugging in:

$$Total\ current\ needed\ [A] = \frac{0.41336\frac{mol}{s} \times 2 \times 96485\frac{sA}{mol}}{1} = 79\ 766\ A \tag{4b}$$

Now, multiplying by cell voltage (1.3 V) to give the power consumed:

$$Power\ Consumed\ [W] = Total\ current\ needed\ [A] \times Cell\ voltage\ [V] = 79\ 766\ A \times 1.3\ V = 103.70\ kW \tag{5}$$

Multiplying by the price of electrolyser and scaling by the current density gives:

$$Total\ Electrolyzer\ Cost\ (\$) = Power\ Consumed\ [kW] \times Electrolyzer\ Cost\ \left[\frac{\$}{kW}\right] \times \frac{base\ current\ density\ \left[\frac{mA}{cm^2}\right]}{input\ current\ density\left[\frac{mA}{cm^2}\right]} \tag{6a}$$

Plugging in our input current density of 800 mA/cm^2 with the base current density of 400 mA cm^{-2}:

$$Total\ Electrolyzer\ Cost\ (\$) = 103.70\ kW \times 250\frac{\$}{kW} \times \frac{400\frac{mA}{cm^2}}{800\frac{mA}{cm^2}} = \$\ 12\ 962.50 \quad (6b)$$

This is an estimate of the total one-time cost for all the electrolyser materials. To find the cost per tonne of CO, we find a yearly cost assuming zero salvage value at the end of the plant's lifetime and divide this by the number of operating days of the plant to find a daily cost. This process is used for all capital costs and starts by calculating a capital recovery factor (*CRF*) based on discount rate, *i*, and the lifetime of the materials.

$$CRF_{electrolyzer} = \frac{i(1+i)^{lifetime}}{(1+i)^{lifetime} - 1} \quad (7a)$$

Plugging in a discount rate of 5% and an assumed lifetime of 30 years for the electrolyser:

$$CRF_{electrolyzer} = \frac{0.05(1.05)^{30}}{(1.05)^{30} - 1} = 0.065051 \quad (7b)$$

Using this *CRF*, we can multiply by our total cost of electrolyser to find an annuity to pay off the plant. We then divide this by the total number of days the plant is operational in a year to find the cost per tonne of CO. We assume the plant operates for 90% of the days in a year, thus giving a capacity factor of 0.9 (This is equivalent to operating 328.5 days a year). This gives us:

$$Electrolyser\ cost\ \left[\frac{\$}{tonne\ CO}\right] = \frac{CRF_{electrolyser} \times Total\ Electrolyser\ Cost\ [\$]}{Capacity\ factor \times 365\left[\frac{days}{year}\right] \times production\left[\frac{tonne\ CO}{day}\right]} \quad (8a)$$

Assuming our capacity factor of 0.9 gives:

$$Electrolyser\ cost\ \left[\frac{\$}{tonne\ CO}\right] = \frac{0.065051 \times \$12\ 962.50}{0.9 \times 365\frac{days}{year} \times 1\frac{tonne\ CO}{day}} = \mathbf{2.57}\ \frac{\$}{\boldsymbol{tonne\ CO}} \quad (8b)$$

This SOEC electrolyser cost is relatively small due to the high current density and the associated savings in electrolyser materials.

Catalyst and Membrane

The catalyst and membrane costs in our model are calculated by assuming their total cost is 5% of the total electrolyser cost. A lifetime of 5 years is used for these components, instead of the 30 years for the electrolyser. For these materials, the CRF is:

$$CRF_{C\&M} = \frac{i(1+i)^{lifetime}}{(1+i)^{lifetime} - 1} = \frac{0.05(1.05)^5}{(1.05)^5 - 1} = 0.23097 \quad (9)$$

Now we can find a price for the catalyst and membrane per tonne of CO:

$$C\ and\ M\ cost\left[\frac{\$}{tonne\ CO}\right] = \frac{CRF_{C\&M} \times Total\ Electrolyser\ Cost\ [\$] \times 0.05}{Capacity\ factor \times 365\left[\frac{days}{year}\right] \times production\left[\frac{tonne\ CO}{day}\right]} \quad (10a)$$

Plugging in values:

$$C\ and\ M\ cost\ \left[\frac{\$}{tonne\ CO}\right] = \frac{0.23097 \times \$12\,962.50 \times 0.05}{0.9 \times 365\,\frac{days}{year} \times 1\,\frac{tonne\ CO}{day}} = \mathbf{0.46}\ \frac{\$}{\boldsymbol{tonne\ CO}} \quad (10b)$$

Electricity Cost

To find the cost of electricity, we can start with our calculation of power consumed from Eq. (5). Using this, we multiply by 24 hours to find the energy required to produce 1 tonne of CO (as our production rate is 1 tonne CO per day) and multiply by the electricity cost. Here, we use an electricity price of 3 ¢ kWh^{-1}, taken from recent onshore wind power auctions.[5] The cost of electricity can be calculated as:

$$Cost\ of\ electricity\ \left[\frac{\$}{tonne\ CO}\right] = \frac{Power\ Cons\ [kW] \times 24h \times electricity\ price\ \left[\frac{\$}{kWh}\right]}{CO\ production\ \left[\frac{tonne\ CO}{day}\right]} \quad (11a)$$

Plugging in values gives:

$$Cost\ of\ electricity\ \left[\frac{\$}{tonne\ CO}\right] = \frac{103.70\ kW \times 24\ h \times \frac{0.03\$}{kWh}}{1\,\frac{tonne\ CO}{day}} = \mathbf{74.66}\ \frac{\$}{\boldsymbol{tonne\ CO}} \quad (11b)$$

Other operating costs

This component adds an additional 10% of our electricity costs to account for maintenance and labour during plant operation.

$$Other\ operating\ costs\ \left[\frac{\$}{tonne\ CO}\right] = Cost\ of\ electricity\ \left[\frac{\$}{tonne\ CO}\right] \times 0.1 \quad (12a)$$

This gives:

$$Other\ operating\ costs\ \left[\frac{\$}{tonne\ CO}\right] = 74.66\ \frac{\$}{tonne\ CO} \times 0.1 = \mathbf{7.47}\ \frac{\$}{\boldsymbol{tonne\ CO}} \quad (12b)$$

Cathode Separation

For separation on the anode and cathode outputs, a pressure swing adsorption (PSA) separation unit is used based on a model built for biogas upgrading.[6,7] For our TEA, a reference cost of \$1 989 043 per 1000 m^3 $hour^{-1}$ capacity with a scaling factor of 0.7 and electricity requirements given by 0.25 kWh m^{-3} were used. The capital and operating costs for this system were modelled as:

$$PSA\ Capital\ Cost\ [\$] = \$1\,989\,043 \times \left(\frac{flow\ rate\ \left[\frac{m^3}{hour}\right]}{1000\ \frac{m^3}{hour}}\right)^{0.7} \quad (13)$$

$$PSA\ Operating\ Cost\ \left[\frac{\$}{tonne\ CO}\right] = 0.25\ \frac{kWh}{m^3} \times flow\ rate\left[\frac{m^3}{hour}\right] \times 24\frac{hour}{day} \times electricity\ price\left[\frac{\$}{kWh}\right] \quad (14)$$

To calculate these costs, we must find the flow rate at the cathode output. This is done by first finding the flow rate of produced CO per hour assuming an ideal gas, standard conditions, and a constant rate of production. Although the gases inside the electrolyser are held at 800 °C, we assume here that there is sufficient time and tubing for the cathode output to return to room temperature before it enters the PSA unit:

$$Output\ CO\ flow\ rate\ \left[\frac{m^3}{hour}\right] = \frac{10^6\ g \times 8.314\ Jmol^{-1}K^{-1} \times 298K}{28\frac{g}{mol} \times 101\ 300\ Pa \times 24\frac{hour}{day}} = 36.395\ \frac{m^3}{hour} \quad (15)$$

Now, assuming constant pressure, we can find the flow rate of CO_2 out of the cathode using a given single-pass conversion. Note: this single-pass conversion must be updated if CO_2 is lost to carbonate formation and only represents the amount of CO_2 that is reduced to any product vs the CO_2 that passes through the cathode stream, unreacted. Since there is no carbonate formed in the SOEC, we can use the overall single-pass conversion of 40% for this conversion metric:

$$Output\ CO_2\ flow\ rate\ \left[\frac{m^3}{hour}\right] = \frac{CO\ flowrate\ \left[\frac{m^3}{hour}\right] \times molar\ ratio\ \left[\frac{CO_2}{CO}\right]}{\frac{singlepass\ conversion[\%]}{100}} \times \left(\frac{100 - singlepass\ conversion[\%]}{100}\right) \quad (16a)$$

Plugging in values gives:

$$Output\ CO_2\ flowrate\ \left[\frac{m^3}{hour}\right] = \frac{36.395\frac{m^3}{hour} \times 1}{\frac{40}{100}} \times \frac{100 - 40}{100} = 54.593\ \frac{m^3}{hour} \quad (16b)$$

Next, we use our assumption that the only other product is H_2. We can find the amount of current that goes towards H_2 as:

$$Current\ towards\ H_2[A] = Total\ current\ needed[A] \times \frac{100 - FE_{CO}[\%]}{100} \quad (17a)$$

However, since we are using a FE of 100% for the SOEC, there will be no H_2 in the cathode output stream. We still include the calculation here as it is required for all other systems in our TEA.

$$Current\ towards\ H_2[A] = 79766\ A \times 0 = 0\ A \tag{17b}$$

In other systems, we would now find the moles of H_2 produced per hour:

$$H_2\ production\ \left[\frac{mol}{hour}\right] = \frac{Current\ towards\ H_2[A] \times 3600\frac{s}{hour}}{2\frac{electrons}{H_2\ product} \times Faraday's\ Constant} \tag{18a}$$

$$H_2\ production\ \left[\frac{mol}{hour}\right] = \frac{0\ A \times 3600\frac{s}{hour}}{2\frac{electrons}{H_2\ product} \times 96485\frac{sA}{mol}} = 0\ \frac{mol}{hour} \tag{18b}$$

Assuming standard conditions and an ideal gas, we can find the flow rate in $m^3\ hour^{-1}$:

$$flowrate_{H2}\left[\frac{m^3}{hour}\right] = \frac{H_2\ production\left[\frac{mol}{hour}\right] \times 8.314\frac{J}{mol \times K} \times 298K}{101.3 \times 10^3 Pa} \tag{19a}$$

$$flow\ rate_{H2}\left[\frac{m^3}{hour}\right] = \frac{0\frac{mol}{hour} \times 8.314\frac{J}{mol \times K} \times 298K}{101.3 \times 10^3 Pa} = 0\ \frac{m^3}{hour} \tag{19b}$$

Now, we can find our final flow rate by adding Eqs. (15), (16b), and (19b):

$$flow\ rate\ \left[\frac{m^3}{hour}\right] = (36.395 + 54.592 + 0)\frac{m^3}{hour} = 90.988\frac{m^3}{hour} \tag{20}$$

Using this, we calculate our capital and operating costs using Eq. (13) and (14):

$$PSA\ Capital\ Cost\ [\$] = \$1\ 989\ 043 \times \left(\frac{90.988\frac{m^3}{hour}}{1000\ \frac{m^3}{hour}}\right)^{0.7} = \$371\ 477.96 \tag{13a}$$

$$PSA\ Operating\ Cost\ \left[\frac{\$}{tonne\ CO}\right] = 0.25\ \frac{kWh}{m^3} \times 90.988\frac{m^3}{hour} \times 24\frac{hour}{day} \times 0.03\frac{\$}{kWh} = \mathbf{16.38}\ \frac{\$}{\boldsymbol{tonne}\ \mathbf{CO}} \tag{14a}$$

Finally, we can find the capital cost per tonne of CO by adapting Eq. (8a) and assuming the same lifetime as the electrolyser (30 years):

$$PSA\ Capital\ Cost\ \left[\frac{\$}{tonne\ CO}\right] = \frac{CRF_{electrolyzer} \times PSA\ Capital\ Cost\ [\$]}{Capacity\ factor \times 365\left[\frac{days}{year}\right] \times production\left[\frac{tonne\ CO}{day}\right]} \quad (21a)$$

$$PSA\ Capital\ Cost\ \left[\frac{\$}{tonne\ CO}\right] = \frac{0.065051 \times \$\ 371\ 477.96}{0.9 \times 365\frac{days}{year} \times 1\frac{tonne\ CO}{day}} = \mathbf{73.56}\ \frac{\$}{\boldsymbol{tonne\ CO}} \quad (21b)$$

Heating

The SOEC in our system is modelled at high temperature. By running at high temperature, we must include the costs associated with heating the system and bringing the inputs to temperature. For this, we consider heating input CO_2 and the electrolyser cell (nichrome was assumed to be the material) to 800 °C from 25 °C with a heating efficiency of 50%. Note: we report heating costs per tonne of CO which is easy to do for CO_2 as it is continuously flowing. However, for the electrolyser, it is unclear how much heating is required to keep it at temperature as this depends on its insulation from the surrounding environment. Due to this uncertainty, we assume that the electrolyser needs to be heated from 25 °C to 800 °C for every tonne of CO produced. For CO_2 and the nichrome (which do not have a phase change in this temperature range), the energy required to heat can be calculated as:

$$Energy\ to\ heat\ [J] = Heat\ Capacity\ \left[\frac{J}{kg \times K}\right] \times \Delta T[K] \times mass[kg] \quad (22a)$$

For CO_2, with a heat capacity of 843 J/(kg K) in gas form, we can find the mass of CO_2 required to heat for 1 tonne of output CO from Eq. (1b) and divide by the single-pass conversion to account for unreacted CO_2:

$$Input\ Mass_{CO2}\left[\frac{kg\ CO_2}{tonne\ CO}\right] = \frac{1000\ kg\ CO \times 44\frac{g}{mol}}{28\frac{g}{mol}} \times \frac{1}{single\ pass\ conversion\ [decimal]} \quad (1c)$$

$$Input\ Mass_{CO2}\left[\frac{kg\ CO_2}{tonne\ CO}\right] = \frac{1000\ kg\ CO \times 44\frac{g}{mol}}{28\frac{g}{mol}} \times \frac{1}{0.4} = 3928.58\ \frac{kg\ CO_2}{tonne\ CO} \quad (1d)$$

For nichrome, we can find the mass required to bring to temperature by assuming a constant electrolyser thickness of 5 cm. Then, by multiplying by the total area required and the density of nichrome (8400 kg m^{-3}), we get the total mass. To do this, we start with the total current needed for the SOEC cell to produce 1 tonne of CO per day using Eq. (4b). We can use this to find the surface area needed:

$$Surface\ area\ of\ electrolyzer\ [m^2] = \frac{Total\ current\ needed\ [mA]}{Current\ density\ \left[\frac{mA}{cm^2}\right] \times \left(\frac{100cm}{1m}\right)^2} \quad (23a)$$

$$Surface\ area\ of\ electrolyzer\ [m^2] = \frac{79\ 766\ 000\ mA}{800\ \frac{mA}{cm^2} \times \left(\frac{100cm}{1m}\right)^2} = 9.9708\ m^2 \quad (23b)$$

Finally, we can use the surface area to find the total mass of nichrome:

$$Mass_{nichrome}[kg] = Surface\ area\ of\ electrolyzer\ [m^2] \times thickness[m] \times density\left[\frac{kg}{m^3}\right] \quad (24a)$$

$$Mass_{nichrome}[kg] = 9.9708\ m^2 \times 0.05m \times 8400\ \frac{kg}{m^3} = 4187.7\ kg \quad (24b)$$

Now that we have the mass of CO_2 and nichrome required to heat per tonne of CO, we can calculate the energy required using Eq. (22a):

$$Energy\ to\ heat_{CO2}\left[\frac{J}{tonne\ CO}\right] = Heat\ Capacity_{CO2}\left[\frac{J}{kg \times K}\right] \times \Delta T[K] \times Mass_{CO2}\left[\frac{kg}{tonne\ CO}\right] \quad (22a)$$

$$Energy\ to\ heat_{CO2}\left[\frac{GJ}{tonne\ CO}\right] = 843\ \frac{J}{kg \times K} \times (800 - 25)K \times 3928.58\ \frac{kg\ CO_2}{tonne\ CO} = 2.5666 \frac{GJ}{tonne\ CO} \quad (22b)$$

Now for nichrome:

$$Energy\ to\ heat_{nichrome}\left[\frac{GJ}{tonne\ CO}\right] = 460 \frac{J}{kg \times K} \times (800 - 25)K \times 4187.7\ kg = 1.4929\ \frac{GJ}{tonne\ CO} \quad (22c)$$

We can find the cost of heating these materials by using the cost of electricity (0.03 \$ kWh^{-1}) and a heating efficiency of 50%:

$$Heating\ Cost_{CO2}\left[\frac{\$}{tonne\ CO}\right] = Energy\ to\ heat_{CO2}\left[\frac{GJ}{tonne\ CO}\right] \times \frac{1\ kWh}{0.0036\ GJ} \times Electricity\ Price\left[\frac{\$}{kWh}\right] \times \frac{1}{Heating\ efficiency[\%]} \quad (25a)$$

$$Heating\ Cost_{CO2}\left[\frac{\$}{tonne\ CO}\right] = 2.5666\ \frac{GJ}{tonne\ CO} \times \frac{1\ kWh}{0.0036\ GJ} \times 0.03\ \frac{\$}{kWh} \times \frac{1}{0.5} = \mathbf{42.78}\ \frac{\$}{\mathbf{tonne\ CO}} \quad (25b)$$

$$Heating\ Cost_{nichrome}\left[\frac{\$}{tonne\ CO}\right] = 1.4929\ \frac{GJ}{tonne\ CO} \times \frac{1\ kWh}{0.0036\ GJ} \times 0.03 \frac{\$}{kWh} \times \frac{1}{0.5} = \mathbf{24.88}\ \frac{\$}{\boldsymbol{tonne\ CO}} \quad (25c)$$

Balance of Plant and Installation Costs

To account for peripheral equipment surrounding the electrolyser, we can estimate a Balance of Plant (BoP) cost by adding 50% of all capital costs to the final cost of CO. Similarly, we can estimate installation costs by using a Lang factor of 1. As a result, we will add 1.5 times the current capital costs to estimate these additional costs. Note: to find the total capital costs, we will add the cost of electrolyser, catalyst and membrane, anode separation capital, and cathode separation capital:

$$Total\ Capital\ Costs\ \left[\frac{\$}{tonne\ CO}\right] = (2.57 + 0.46 + 73.56 + 0\ ) \frac{\$}{tonne\ CO} = 76.59\ \frac{\$}{tonne\ CO} \quad (26)$$

$$BoP\ \left[\frac{\$}{tonne\ CO}\right] = BoP\ Factor \times Total\ Capital\ Costs \left[\frac{\$}{tonne\ CO}\right] \quad (27a)$$

$$BoP \left[\frac{\$}{tonne\ CO}\right] = 0.5 \times 76.59 \frac{\$}{tonne\ CO} = \mathbf{38.30}\ \frac{\$}{\boldsymbol{tonne\ CO}} \quad (27b)$$

Now, installation costs:

$$Installation\ Cost\ \left[\frac{\$}{tonne\ CO}\right] = Lang\ Factor \times\ Total\ Capital\ Costs \left[\frac{\$}{tonne\ CO}\right] \quad (28a)$$

$$Installation\ Cost\ \left[\frac{\$}{tonne\ CO}\right] = 1 \times 76.59 \frac{\$}{tonne\ CO} = \mathbf{76.59}\ \frac{\$}{\boldsymbol{tonne\ CO}} \quad (28b)$$

Final Summation

Now, we can sum all the bolded costs above to find the total cost of producing 1 tonne of CO:

$$\boldsymbol{Cost\ of\ CO}\left[\frac{\$}{\boldsymbol{tonne\ CO}}\right] = \mathbf{404.77}\ \frac{\$}{\boldsymbol{tonne\ CO}} \quad (29)$$

The next sections will focus on the MEA systems, including the cost of electrolyte, anode separation of crossover CO_2 from OER O_2, and regeneration of CO_2 and electrolyte that was lost to KOH in the single-

step CO_2-to-C_2H_4 system. Note that all costs below will be reported per tonne of ethylene as relevant for both CO_2RR to ethylene or CORR to ethylene systems.

Anode Separation (MEA cell only)

The anode separation uses the same model for a PSA separation module as the cathode separation, but this time separates CO_2 from O_2 depending on the input CO_2 crossover ratio for an MEA cell. For an alkaline flow cell and SOEC, we assume there is zero cost associated with anode separation as only O_2 will exit the anode output stream. We will start by finding the flow rate of O_2 out of the anode while assuming standard conditions, ideal gases, and constant pressure:

$$Output\ C_2H_4\ flowrate\ \left[\frac{m^3}{hour}\right] = \frac{10^6\ g \times 8.314\ Jmol^{-1}K^{-1} \times 298K}{28\frac{g}{mol} \times 101\ 300\ Pa \times 24\frac{hour}{day}} = 36.395\ \frac{m^3}{hour} \tag{30}$$

$$flow\ rate_{O2}\left[\frac{m^3}{hour}\right] = flowrate_{C2H4}\left[\frac{m^3}{hour}\right] \times mole\ ratio\left[\frac{O_2}{C_2H_4}\right] = 36.395\frac{m^3}{hour} \times 3 = 109.185\frac{m^3}{hour} \tag{31}$$

Now, we can find the flow rate of CO_2 on the anode side due to crossover. For MEA, we have calculated that approximately 3 molecules of CO_2 crossover for every molecule of CO_2 that is reduced to target product. This assumption comes from a theoretical limitation of neutral MEA electrolysers. In neutral MEA electrolysers, producing 1 mole of C_2H_4 through CO_2RR generates 12 moles of OH^-, which reacts with CO_2 and poses a limit of 25% for CO_2 single-pass conversion in CO_2-to-C_2H_4 conversion.[8] Therefore, we can write the flow rate of CO_2 as:

$$flowrate_{CO2}\left[\frac{m^3}{hour}\right] = flowrate_{C2H4}\left[\frac{m^3}{hour}\right] \times mole\ ratio\left[\frac{CO_2}{C_2H_4}\right] \times crossover\left[\frac{crossover\ CO_2}{reduced\ CO_2}\right] \tag{32a}$$

Plugging in our crossover ratio:

$$flowrate_{CO2}\left[\frac{m^3}{hour}\right] = 36.395\frac{m^3}{hour} \times 2 \times 3 = 218.37\ \frac{m^3}{hour} \tag{32b}$$

Summing these flow rates gives the total flow rate out of the anode:

$$Total\ anode\ flowrate\ \left[\frac{m^3}{hour}\right] = flowrate_{CO2}\left[\frac{m^3}{hour}\right] + flowrate_{O2}\left[\frac{m^3}{hour}\right] \tag{33a}$$

$$Total\ anode\ flowrate\left[\frac{m^3}{hour}\right] = (218.37 + 109.185)\frac{m^3}{hour} = 327.555\ \frac{m^3}{hour} \tag{33b}$$

Now that we have the total flow rate, we can calculate the operating and capital costs using Eq. (13) and (14):

$$PSA\ Capital\ Cost\ [\$] = \$1\ 989\ 043 \times \left(\frac{327.555\ \frac{m^3}{hour}}{1000\ \frac{m^3}{hour}} \right)^{0.7} = \$910\ 632.48 \quad (34)$$

$$PSA\ Operating\ Cost\ \left[\frac{\$}{tonne\ C_2H_4}\right] = 0.25\ \frac{kWh}{m^3} \times 327.555\ \frac{m^3}{hour} \times 24\ \frac{hour}{day} \times 0.03\ \frac{\$}{kWh} = \mathbf{58.96}\ \frac{\$}{\boldsymbol{tonne\ C_2H_4}} \quad (35)$$

Finally, we can find the capital costs per tonne of ethylene using Eq. (8a) and assuming a lifetime of 30 years again (the same as the electrolyser):

$$PSA\ Capital\ Cost\ \left[\frac{\$}{tonne\ C_2H_4}\right] = \frac{CRF_{electrolyser} \times PSA\ Capital\ Cost\ [\$]}{Capacity\ factor \times 365\left[\frac{days}{year}\right] \times production\left[\frac{tonne\ C_2H_4}{day}\right]} \quad (36a)$$

$$PSA\ Capital\ Cost\ \left[\frac{\$}{tonne\ C_2H_4}\right] = \frac{0.065051 \times \$910\ 632.48}{0.9 \times 365\ \frac{days}{year} \times 1\ \frac{tonne\ C_2H_4}{day}} = \mathbf{180.33}\ \frac{\$}{\boldsymbol{tonne\ C_2H_4}} \quad (36b)$$

Carbonate regeneration (Alkaline flow cell only)

Although it is not required in neutral systems, the regeneration of CO_2 and electrolyte for alkaline flow cell electrolysers (which commonly use high concentration KOH) contributes to the final cost of C_2H_4 significantly. For our alkaline flow cell with 3 M KOH, it was estimated that 20 CO_2 molecules reacted with KOH to form carbonate for every CO_2 molecule that was reduced to target product. This assumption comes from experimental measurements in lab-scale cells in which we analyzed the CO_2 flow rate discrepancy between the cathode inlet and cathode outlet for a specific current density. Using this flow rate, the current density, and FE distribution, we calculated the ratio of CO_2 lost to CO_2 reacted. To calculate the cost required to regenerate this much CO_2 and KOH, a model obtained from Aspen Plus by Keith et al. reported energy requirements to regenerate CO_2 from a calcium caustic loop.[9] This loop has three steps: a pellet reactor which uses 27 kWh tonne^{-1} CO_2, a calciner which uses 4.05 GJ tonne^{-1} of CO_2, and a slaker which uses 77 kWh tonne^{-1} CO_2. Adding all these components together gives us 1229 kWh tonne^{-1} CO_2. Using this model, we can calculate the cost of running this system by:

$$Reduced\ CO_2\ [tonne] = \frac{Production\ of\ C_2H_4\left[\frac{tonne}{day}\right] \times mole\ ratio\left[\frac{CO_2}{C_2H_4}\right] \times molecular\ weight_{CO2}}{molecular\ weight_{C2H4}\left[\frac{g}{mol}\right]} \quad (37a)$$

$$Reduced\ CO_2\ [tonne] = \frac{1\ \frac{tonne}{day} \times 2 \times \frac{44g}{mol}}{\frac{28g}{mol}} = 3.1429\ tonne \quad (37b)$$

$$CO_2\ lost\ to\ KOH\ [tonne] = Reduced\ CO_2\ [tonne] \times carbonate\ formation\ \left[\frac{CO_2\ reacting\ with\ KOH}{CO_2\ reduced}\right] \quad (38a)$$

$$CO_2\ lost\ to\ KOH\ [tonne] = 3.1429\ tonne \times 20 = 62.858\ tonne \quad (38b)$$

Now we can find the energy required to regenerate this much CO_2:

$$Energy\ required\ [kWh] = CO_2 lost\ to\ KOH [tonne] \times 1229 \frac{kWh}{tonne\ CO_2} \quad (39a)$$

$$Energy\ required\ [kWh] = 62.858 \times 1229 = 77\ 252\ kWh \quad (39b)$$

We can find the operating cost of the system by multiplying by the electricity price:

$$Operating\ Cost\ \left[\frac{\$}{tonne\ C_2H_4}\right] = Energy\ required [kWh] \times Electricity\ price\ \left[\frac{\$}{kWh}\right] \quad (40a)$$

$$Operating\ Cost\ \left[\frac{\$}{tonne\ C_2H_4}\right] = 77\ 252\ kWh \times 0.03 \frac{\$}{kWh} = \mathbf{2317.56}\ \frac{\$}{\mathbf{tonne\ C_2H_4}} \quad (40b)$$

Input H_2O (MEA and flow cell)

We calculate the cost of input water assuming no water can be recovered from the anode output or that recovering it would be more expensive than buying new water. Therefore, for CO_2RR we calculate buying 6 moles of water for every mole of C_2H_4 produced.

The calculation for the neutral MEA is:

$$H_2O\ required\ \left[\frac{tonne\ H_2O}{tonne\ C_2H_4}\right] = C_2H_4\ output\ \left[tonne \frac{C_2H_4}{day}\right] \times \frac{molecular\ weight_{H2O}\left[\frac{g}{mol}\right]}{molecular\ weight_{C2H4}\left[\frac{g}{mol}\right]} \times molar\ ratio\ \left[\frac{H_2O}{C_2H_4}\right] \quad (41a)$$

Plugging in gives:

$$H_2O\ required\ \left[\frac{tonne\ H_2O}{tonne\ C_2H_4}\right] = 1\ tonne\frac{C_2H_4}{day} \times \frac{18\frac{g}{mol}}{28\frac{g}{mol}} \times 6 = 3.8571\ \frac{tonne\ H_2O}{tonne\ C_2H_4} \quad (41b)$$

Finally, multiplying by the cost of water gives the cost per tonne of ethylene. The cost of water was estimated based on 2019 water rates for the city of Toronto, Canada that listed 3.9549 $CAD m^{-3}.[10] Based on this, we used a value of 5 $ $tonne^{-1}$ as a more conservative estimate for different regions. The final cost of water per tonne of ethylene in our model is:

$$Cost\ of\ input\ H_2O\left[\frac{\$}{tonne\ C_2H_4}\right] = 5\ \frac{\$}{tonne\ H_2O} \times 3.8571\frac{tonne\ H_2O}{tonne\ C_2H_4} = \mathbf{19.29}\ \frac{\$}{\boldsymbol{tonne\ CO}} \quad (42)$$

Electrolyte costs

For our SOEC cell, we assume we are not using an electrolyte. However, we will show the calculation for a MEA cell using 0.1 M $KHCO_3$ at a cost of 750 $ $tonne^{-1}$ and by using a fixed volume factor of 100 L electrolyte m^{-2} of electrolyser, approximated from common lab-scale experiments. The cost is calculated by:

$$Surface\ area\ of\ electrolyser\ [m^2] = \frac{Total\ current\ needed\ [mA]}{Current\ density\ \left[\frac{mA}{cm^2}\right] \times \left(\frac{100cm}{1m}\right)^2} \quad (43a)$$

Plugging in our base case values gives (note the required current is different from the SOEC case above):

$$Surface\ area\ of\ electrolyser\ [m^2] = \frac{797\ 660\ 000\ mA}{150\frac{mA}{cm^2} \times \left(\frac{100cm}{1m}\right)^2} = 531.77\ m^2 \quad (43b)$$

Now we can find the volume of electrolyte required:

$$Volume\ of\ electrolyte\ [L] = Surface\ area\ [m^2] \times 100\ \left[\frac{L}{m^2}\right] = 531.77\ m^2 \times 100\ \frac{L}{m^2} = 53\ 177\ L \quad (44)$$

With this volume, the molecular weight of potassium bicarbonate (100 g mol^{-1}), and the molarity of the anolyte, we can find the mass of potassium bicarbonate required:

$$Mass\ of\ anolyte\ salt\ [g] = Anolye\ molarity\ \left[\frac{mol}{L}\right] \times Anolyte\ volume\ [L] \times molecular\ weight\ \left[\frac{g}{mol}\right] \quad (45a)$$

This gives:

$$Mass\ of\ anolyte\ salt\ [g] = 0.1\ M\ \times 53\ 177\ L\ \times 100\frac{g}{mol} = 531\ 770\ g \quad (45b)$$

The total cost of anolyte is found by multiplying by the price of potassium bicarbonate and the price of water (5 $ $tonne^{-1}$):

$$Cost\ of\ anolyte\ [\$] = mass\ of\ salt\ [tonne] \times price\ of\ salt\ \left[\frac{\$}{tonne}\right] + water\ volume[L] \times water\ price\ \left[\frac{\$}{kg}\right] \quad (46a)$$

This gives:

$$Cost\ of\ anolyte\ [\$] = 0.531770\ tonne \times 750\ \frac{\$}{tonne} + 53\ 177\ L \times 0.005\ \frac{\$}{kg} = \$664.71 \quad (46b)$$

Now, to find the cost of anolyte per tonne of ethylene, we can find a new capital recovery factor assuming the electrolyte has a lifetime of 1 year:

$$CRF_{anolyte} = \frac{0.05(1.05)^1}{1.05^1 - 1} = 1.05 \quad (47)$$

Finally, we can find the cost per tonne of ethylene using the same method as in Eq. (8):

$$Cost\ of\ anolyte\ \left[\frac{\$}{tonne\ C_2H_4}\right] = \frac{CRF_{anolyte} \times Cost\ of\ anolyte\ [\$]}{Capacity\ factor \times 365\ \left[\frac{days}{year}\right] \times production\ \left[\frac{tonne\ C_2H_4}{day}\right]} \quad (48a)$$

Plugging in values gives our final cost per tonne of ethylene:

$$Cost\ of\ anolyte\ \left[\frac{\$}{tonne\ C_2H_4}\right] = \frac{1.05 \times \$664.71}{0.9 \times 365\frac{days}{year} \times 1\frac{tonne\ C_2H_4}{day}} = \mathbf{2.12}\ \frac{\$}{\boldsymbol{tonne\ C_2H_4}} \quad (48b)$$

Note that for alkaline flow cells, a 3 M KOH anolyte was used with a cost of 1000 \$ tonne^{-1}.

Summary of Inputs for all systems:

For all the C_2H_4 producing systems being compared through TEA, we have selected two economic scenarios (a "base case" and an "ideal case"). These provide for systems with performance metrics currently achieved at the lab-scale ("base case") and for reasonable improvements in performance that may be expected in the next few years ("ideal case"). The "base case" metrics for CO_2-to-CO conversion in solid oxide electrolyser cells (SOECs) have been well-established in lab studies.[7] Similarly, the "base case" CO_2RR parameters were taken from the reports with the highest performance metrics (energy efficiency, current density, selectivity, and single pass utilization) reported to date for the neutral MEA (CO_2RR MEA)[1] and alkaline flow cell (CO_2RR flow cell)[2] electrolysers. The "ideal case" metrics are estimates of performance levels expected in the upcoming few years.

Base Case:

Parameters	**CO_2RR MEA**	**CO_2RR flow cell**	**CO_2RR SOEC**	**CORR MEA**
Output Product	C_2H_4	C_2H_4	CO	C_2H_4
CO_2 Cost (\$/tonne)	30	30	30	N/A
CO Cost (\$/tonne)	N/A	N/A	N/A	404.77
H_2O Cost (\$/tonne)	5	5	N/A	5

Electricity cost ($/kWh)	0.03	0.03	0.03	0.03
Electrolyser cost ($/kW)	300	300	250	300
Balance of plant (%)	50	50	50	50
Lang factor	1	1	1	1
Capacity factor	0.9	0.9	0.9	0.9
Cell voltage (V)	3.7	2.5	1.3	2.5
Faradaic efficiency (%)	60	60	100	60
Current density (mA/cm^2)	150	150	800	150
Single pass conversion (%)	15	2.86	40	18
CO_2 crossover factor	3	20	0	0
System lifetime (year)	30	30	30	30
Catalyst/membrane lifetime (year)	5	5	5	5
Electrolyte lifetime (year)	1	1	N/A	1
Electrolyte	$KHCO_3$	KOH	N/A	$KHCO_3$
Electrolyte Molarity (mol/L)	0.1	3	N/A	0.1
Electrolyte salt cost ($/tonne)	750	1000	N/A	750
Operation Temperature (°C)	25	25	800	25
Discount Rate (%)	5	5	5	5

N/A. indicates that the item is not applicable.

Ideal Case

Parameters	**CO_2RR MEA**	**CO_2RR flow cell**	**CO_2RR SOEC**	**CORR MEA**
Output Product	C_2H_4	C_2H_4	CO	C_2H_4
CO_2 Cost ($/tonne)	30	30	30	N/A
CO Cost ($/tonne)	N/A	N/A	N/A	292.25
H_2O Cost ($/tonne)	5	5	N/A	5
Electricity cost ($/kWh)	0.03	0.03	0.03	0.03
Electrolyser cost ($/kW)	300	300	250	300
Balance of plant (%)	50	50	50	50
Lang factor	1	1	1	1
Capacity factor	0.9	0.9	0.9	0.9
Cell voltage (V)	3.7	2.5	1.3	2.5
Faradaic efficiency (%)	95	95	100	95
Current density (mA/cm^2)	200	200	800	200
Single pass conversion (%)	23.75	4.52	90	28.5
CO_2 crossover factor	3	20	0	0
System lifetime (year)	30	30	30	30
Catalyst/membrane lifetime (year)	5	5	5	5
Electrolyte lifetime (year)	1	1	N/A	1
Electrolyte	$KHCO_3$	KOH	N/A	$KHCO_3$
Electrolyte Molarity (mol/L)	0.1	3	N/A	0.1
Electrolyte salt cost ($/tonne)	750	1000	N/A	750

Operation Temperature (°C)	25	25	800	25
Discount Rate (%)	5	5	5	5

N/A. indicates that the item is not applicable.

It is important to note that MEA and flow cell electrolysers use a different electrolyser cost from SOEC. The 300 \$ kW^{-1} is based on a 2020 DOE target for water electrolysis hydrogen production and was provided for a 600 mA cm^{-2} cell.[11] Therefore, when using Eq. (6a), the electrolyser cost is changed to 300 \$ kW^{-1} and the base current density is now 600 mA cm^{-2}.

Additionally, when calculating the cathode separation costs for the CO_2RR MEA and alkaline flow cells, one must revise the single-pass conversion in Eq. (16a) to account for CO_2 that was lost to carbonate. Since the conversion in Eq. (16a) expresses the amount of CO_2 that is reduced to the amount of CO_2 that passes through the cathode stream unreacted, we can rewrite Eq. (16a) as:

$$Output\ CO_2\ flow\ rate\ \left[\frac{m^3}{hour}\right] = \frac{C_2H_4\ flow\ rate\ \left[\frac{m^3}{hour}\right] \times molar\ ratio\ \left[\frac{CO_2}{C_2H_4}\right]}{\left(\frac{singlepass\ conversion\ [decimal]}{\frac{1}{crossover\ factor + 1}}\right)} \times \left(1 - \frac{single\ pass\ conversion[decimal]}{\frac{1}{crossover\ factor + 1}}\right) \quad (16c)$$

Note that it is now written with C_2H_4 as the output as there is assumed to be no crossover when producing CO. For the ideal MEA case with a crossover ratio of 3 and a single-pass conversion of 23.75%, this gives:

$$Output\ CO_2\ flow\ rate\ \left[\frac{m^3}{hour}\right] = \frac{36.3955\ \frac{m^3}{hour} \times 2\ \frac{CO_2}{C_2H_4}}{\left(\frac{0.2375}{\frac{1}{3+1}}\right)} \times \left(1 - \frac{0.2375}{\frac{1}{3+1}}\right) = 3.8311\ \frac{m^3}{hour} \quad (16d)$$

Energy Calculations

All energy calculations provided use the same models outlined above, but simply stop before multiplying by the electricity price. For example, for the energy cost of carbonate regeneration, we use Eq. (39) to obtain the energy required to run the calcium cycle. Similarly, for electrolyser energy requirements, Eq.

(6a) divided by the electricity price gives the energy needed to run the system. For separation and SOEC heating, the same approach is used.

Note S3. Further improvements to be made toward profitable C_2H_4 electroproduction. Despite the gains made in this study, achieving profitable ethylene electroproduction in the SOEC:MEA system will require further improvements in the performance metrics of both the first step (CO_2-to-CO in SOEC) and second step (CO-to-C_2H_4 in MEA). Table S20 provides a detailed summary of the input parameters that would enable profitable ethylene production in the cascade CO_2-to-C_2H_4 approach ("SOEC optimistic" and "CORR optimistic"). Potential improvements in the first step (CO_2-to-CO in SOEC) would be (1) increasing the single pass conversion efficiency (to for example 90%), reducing the cost of electricity (to for example 2 c kWh^{-1}), and reducing the cost of electrolyser (to for example 250 \$ kW^{-1}). As the second step (CO-to-C_2H_4 in MEA) makes up the majority of the energy density for producing C_2H_4 from CO_2, further improvements in the performance metrics of the second step (CO-to-C_2H_4 in MEA) will significantly lower the energy density for producing ethylene. For profitable C_2H_4 production, potential improvements in the CO-to-C_2H_4 conversion step would be (1) achieving higher reaction rates (e.g., current densities as high as 1000 mA cm^{-2}), (2) lowering full-cell potential (e.g., cell voltages as low as 1.7 V), (3) achieving higher Faradaic efficiency toward CO-to-C_2H_4 conversion (e.g., CO-to-C_2H_4 selectivities as high as 95%), and (4) achieving higher single pass utilization (e.g., CO_2-to-CO single pass conversion of 95%). Realization of all these goals will require improved CO-to-C_2H_4 catalysts as well as electrolysers – important advances that we hope are motivated by this work. Additionally, a reduction in the cost of electricity (e.g., down to 2 c kWh^{-1}) would significantly decrease the energy required for producing C_2H_4 in the SOEC:MEA electrolyser.

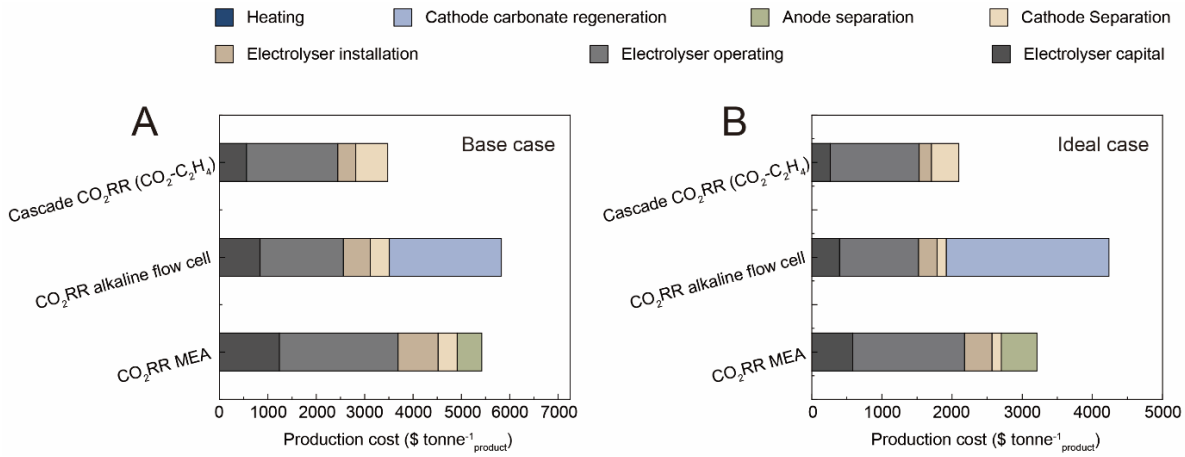


Figure S3. TEA comparison of the production costs in the cascade SOEC-MEA system and the state-of-the-art CO_2-to-C_2H_4 electrolysers. (A) Base-case scenarios. **(B)** Ideal-case scenarios.

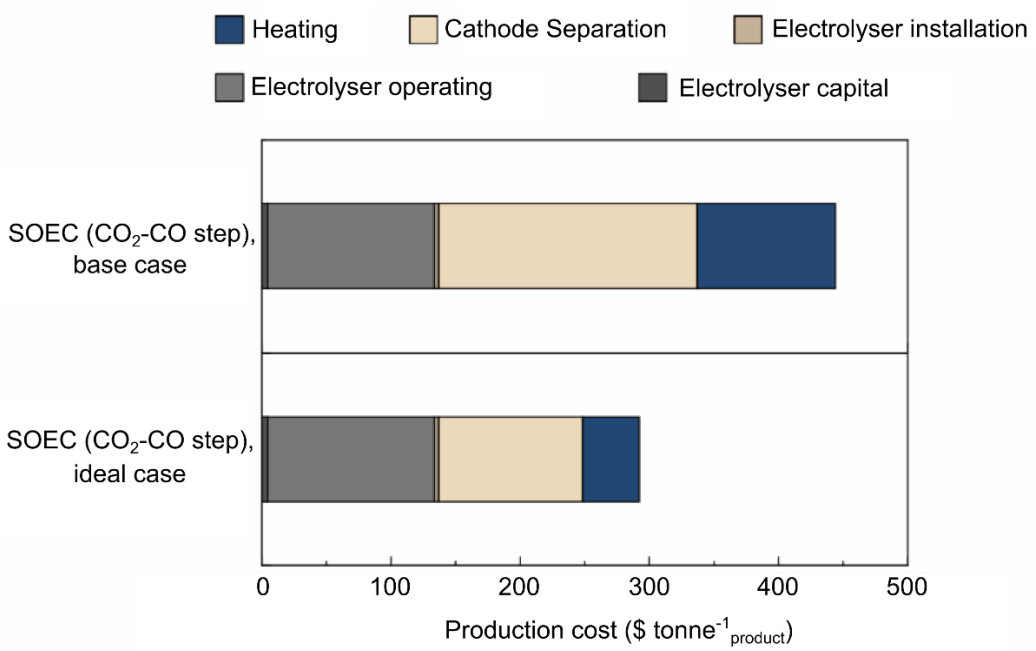


Figure S4. TEA comparison of the CO_2-to-CO electrolysis using SOECs in base and ideal cases.

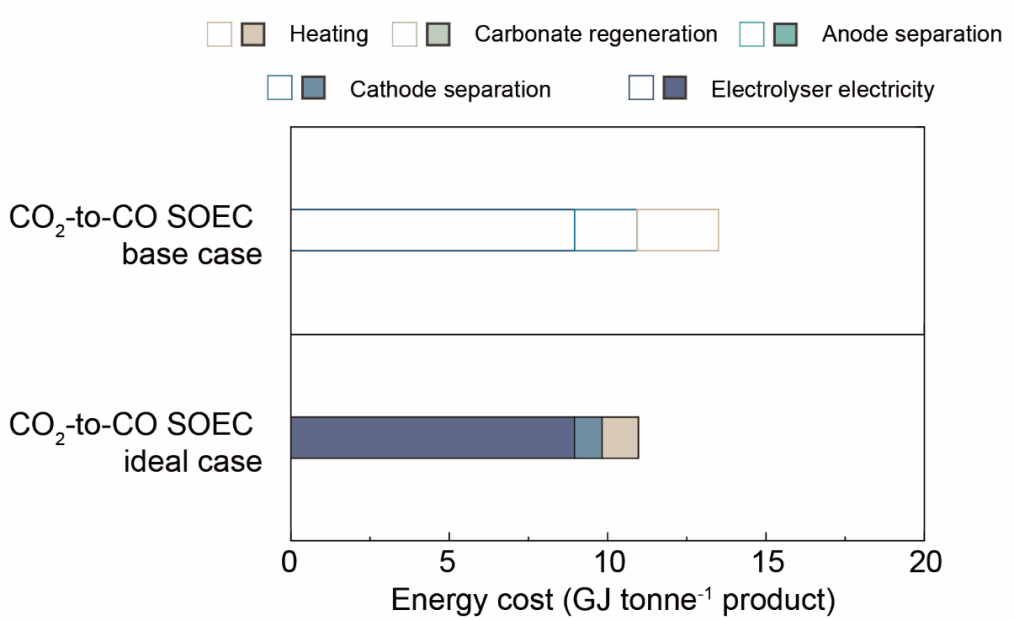


Figure S5. TEA showing detailed SOEC energy cost breakdown for base- and ideal-case scenarios.

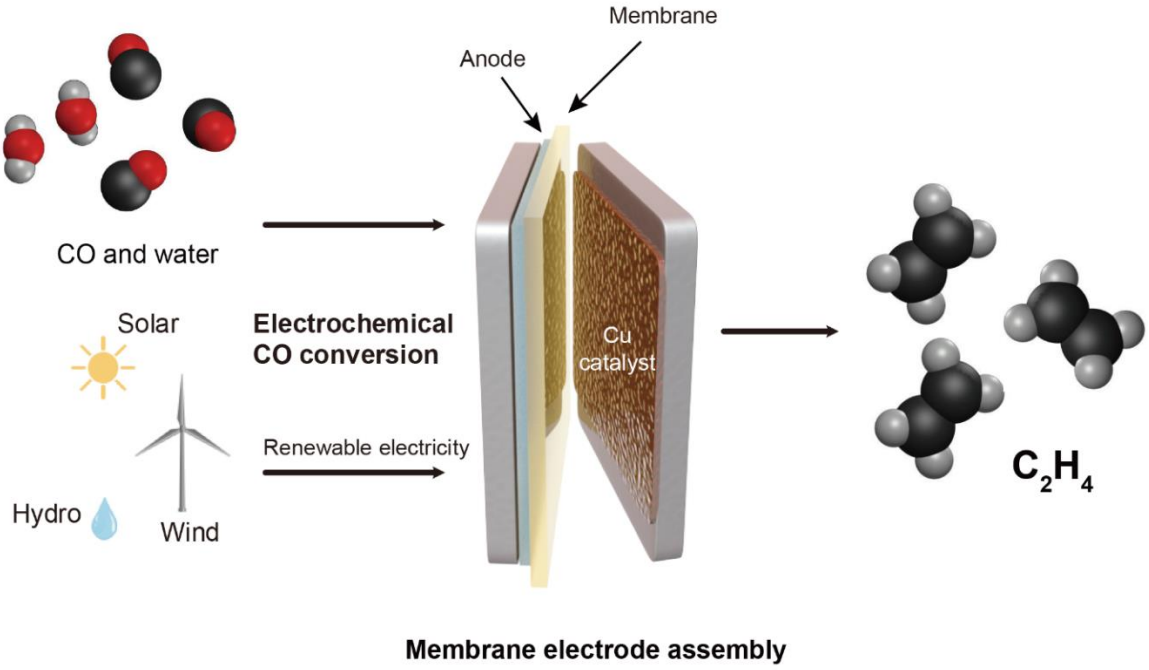
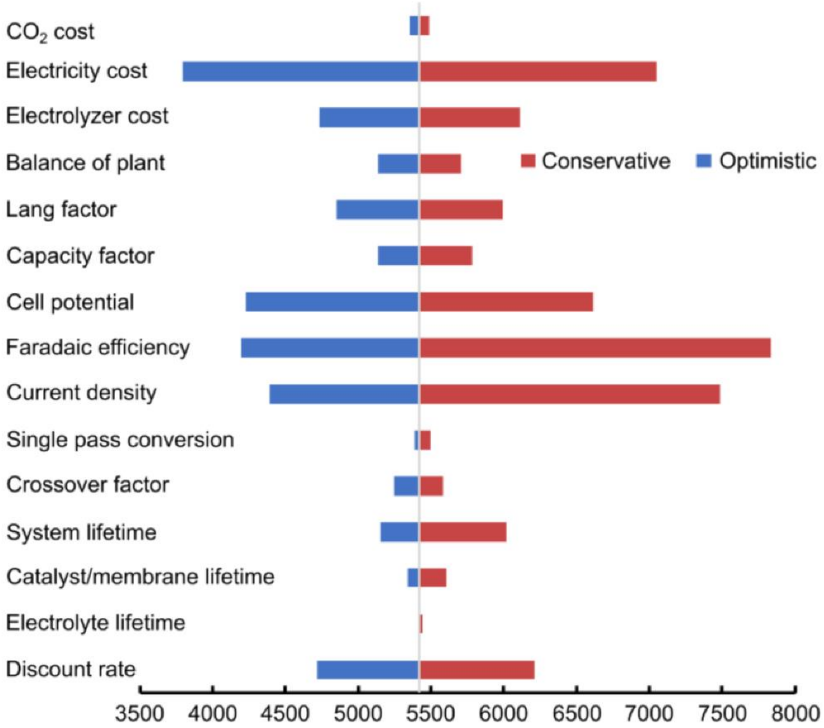


Figure S6. A schematic illustration of CO electroreduction to C_2H_4 in an MEA powered by renewables. The anode is IrO_2 on Ti meshes. In the cascade CO_2RR, the CO-to-C_2H_4 MEA is connected to a CO_2 capture unit at the outlet of the SOEC.

A



B

Parameters	Optimistic	Centre-cost	Conservative
CO_2 Cost ($/tonne)	10	30	50
Electricity cost ($/kWh)	0.01	0.03	0.05
Electrolyser cost ($/kW)	200	300	400
Balance of plant (%)	25	50	75
Lang factor	0.5	1	1.5
Capacity factor	1	0.9	0.8
Cell voltage (V)	2.7	3.7	4.7
Faradaic efficiency (%)	80	60	40
Current density (mA/cm^2)	300	150	75
Single pass conversion (%)	40	15	6.67
CO_2 crossover factor	1	3	5
System lifetime (year)	40	30	20
Catalyst/membrane lifetime (year)	7	5	3
Electrolyte lifetime (year)	2	1	0.1
Discount Rate (%)	2.5	5	7.5

Figure S7. A sensitivity analysis for a single-step MEA electrolyser that converts CO_2-to-C_2H_4. **(A)** A tornado plot showing the sensitivity of the CO_2RR MEA electrolyser **(B)** Input parameters for centre-cost, optimistic and conservative scenarios. The tornado plot shows a sensitivity analysis for a MEA electrolyser that converts CO_2-to-C_2H_4. The centre cost corresponds to the CO_2RR MEA base case provided in Table S1 and a set of conservative and optimistic values were selected to provide a wide range of values for each input. The red (blue) bars represent the increase (decrease) in final cost of C_2H_4 by changing parameter independently from its centre-cost value to its conservative (optimistic) input. All optimistic, conservative, and centre-cost inputs used to create Figure S7A are listed in Figure S7B. In our analyses, we assume an input CO_2 cost = $30/tonne, electricity cost = 3 ¢/kWh, production

rate = 1 tonne/day, balance of plant = 50%, lang factor = 1, capacity factor = 0.9, electrolyser lifetime = 30 years, catalyst and membrane lifetime = 5 years, electrolyte lifetime = 1 year, and discount rate = 5%. Details of how these parameters are incorporated into a final cost/energy calculation are provided in Note S2. These parameters depend greatly on the electrolyser and are difficult to predict. However, we find in our sensitivity analysis here that many of these parameters have small effects on ethylene production and thus were kept constant for all systems.

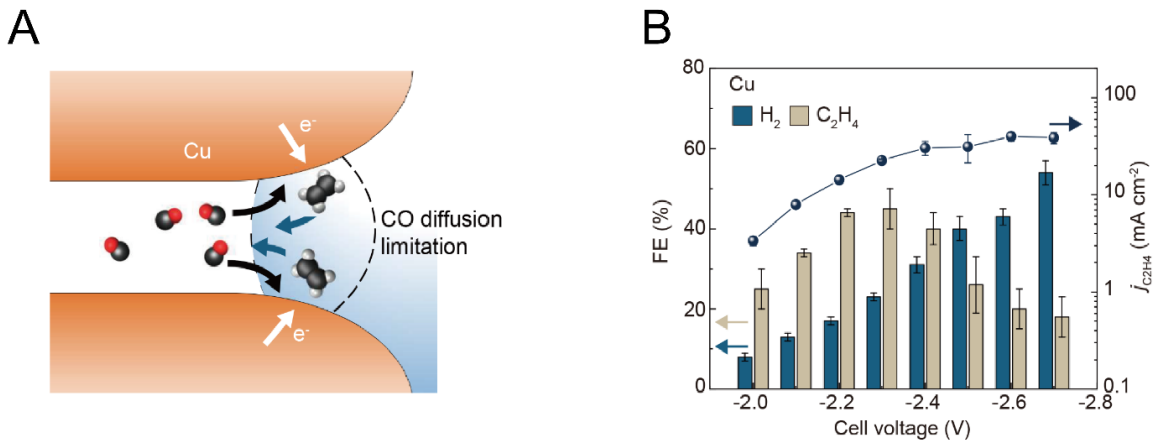


Figure S8. CORR-to-C_2H_4 at the bare Cu surface. (A) The three-phase catalytic interface using a bare Cu catalyst and **(B)** the obtained CO-to-C_2H_4 performance in 3 M KOH anolyte.

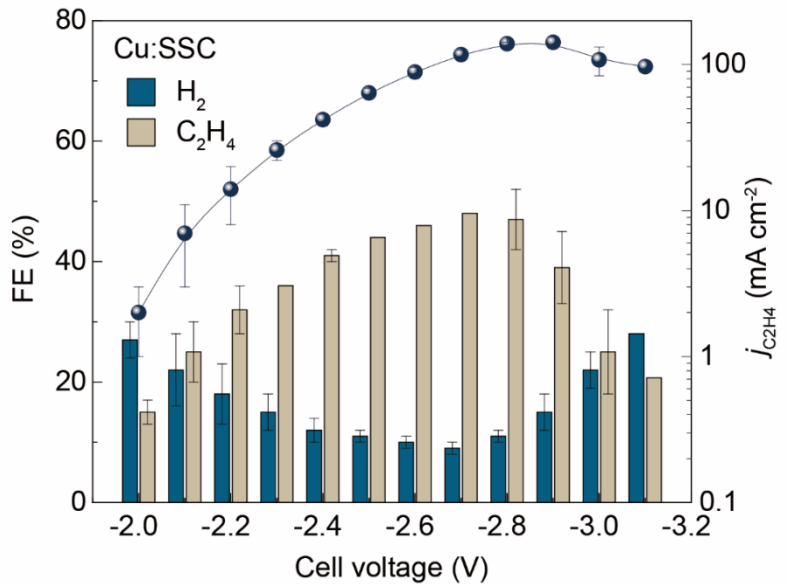


Figure S9. The C_2H_4 FE and partial current density of an MEA using the Cu:SSC cathode. Error bars correspond to the standard deviation of 3 independent measurements.

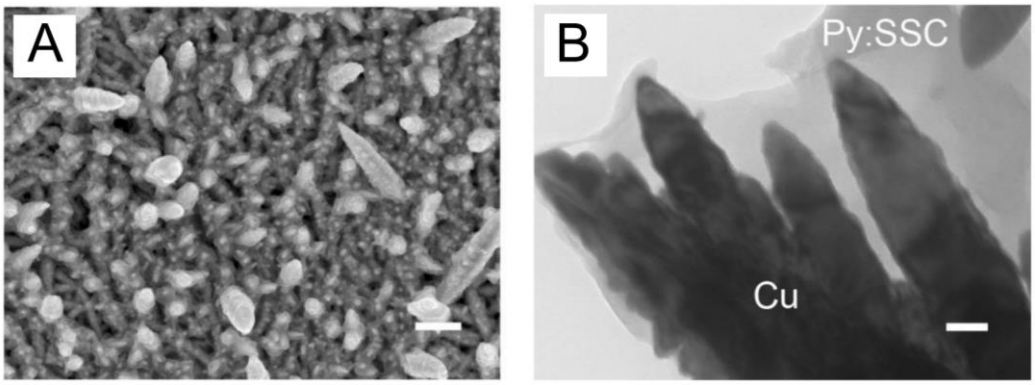


Figure S10. The SEM and TEM images of the Cu:Py:SSC catalysts. Scale bars in **(A,B)** are 1 μm and 50 nm, respectively.

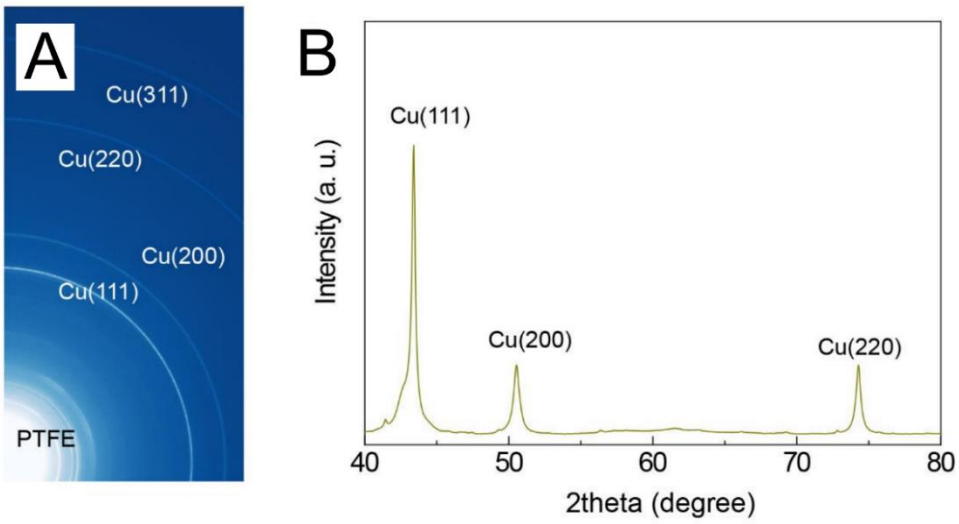


Figure S11. **The crystallinity of the Cu:Py:SSC catalyst. (A)** GIWAXS pattern of the Cu:Py:SSC combination. **(B)** GIWAXS-derived 1D XRD profile of the the Cu:Py:SSC combination.

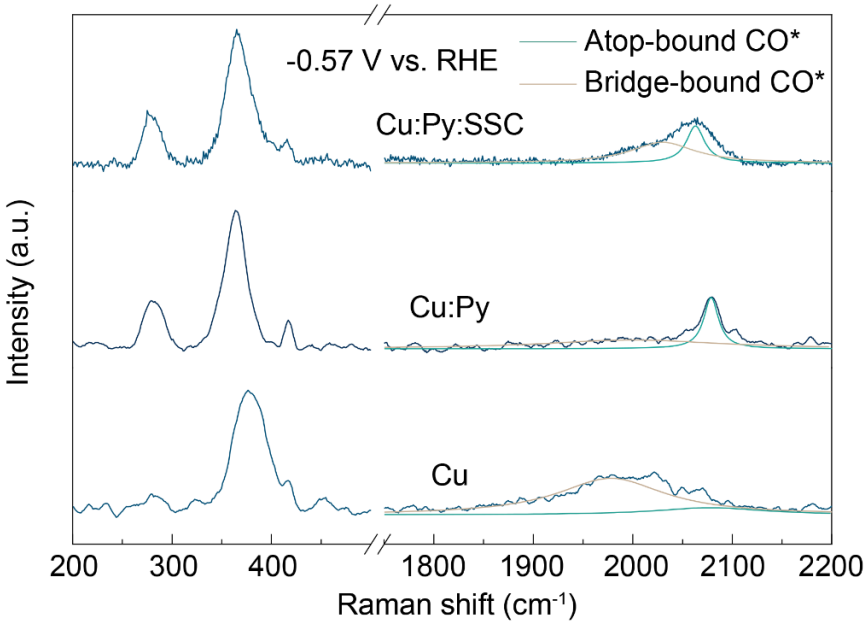


Figure S12. *In-situ* Raman spectra obtained on Cu:Py:SSC, Cu:Py, and bare Cu at -0.57 V vs. RHE. The bare Cu surface is predominated by the bridge-bound CO*. The modification of the Py molecule greatly increased the fraction of the atop-bound CO*. After SSC ionomer coating, large portion of atop-bound CO* was still seen, although the intensity of the bridge-bound CO* increased slightly. Details on the processing of Raman spectra can be found in the experimental section.

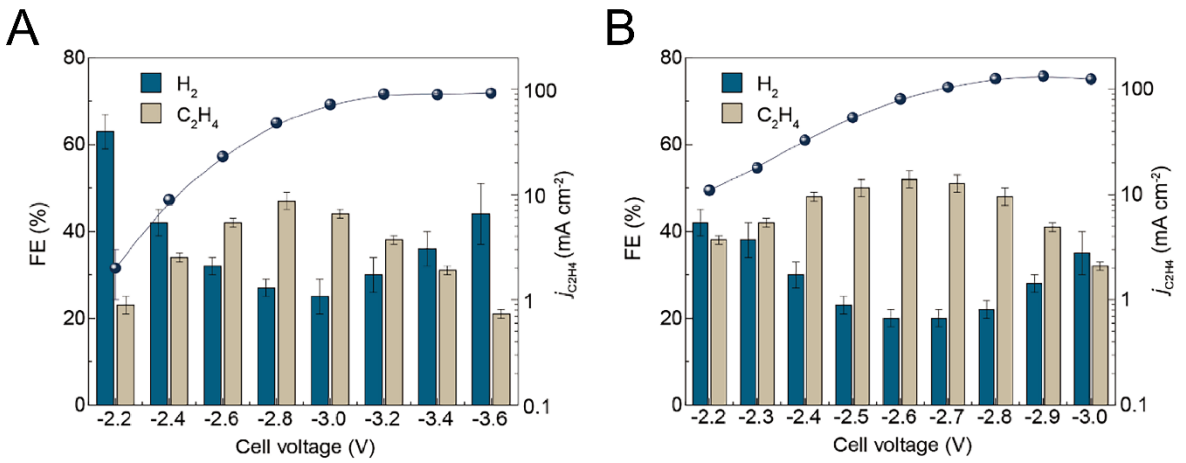


Figure S13. The C_2H_4 FE and partial current density of MEAs using the Cu:Py:SSC cathode. The anolytes are 0.1 and 1 M KOH in **(A)** and **(B)**, respectively. Error bars correspond to the standard deviation of 3 independent measurements.

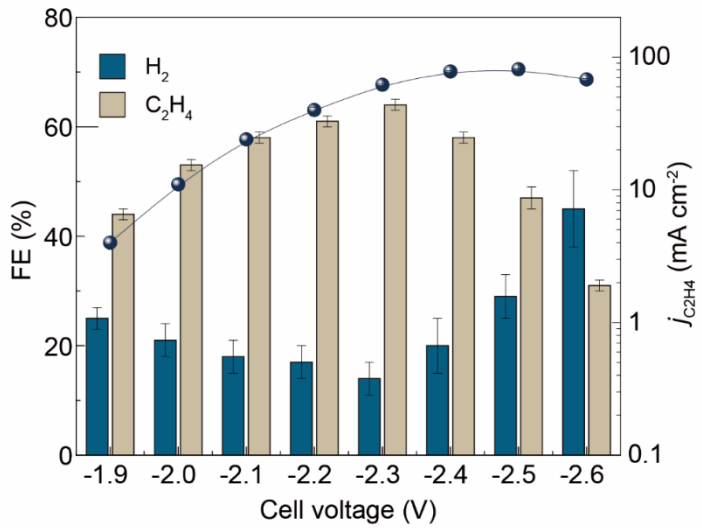


Figure S14. The C_2H_4 FE and partial current density of an MEA using the Cu:Py:SSC cathode and 5 M KOH anolyte. Error bars correspond to the standard deviation of 3 independent measurements.

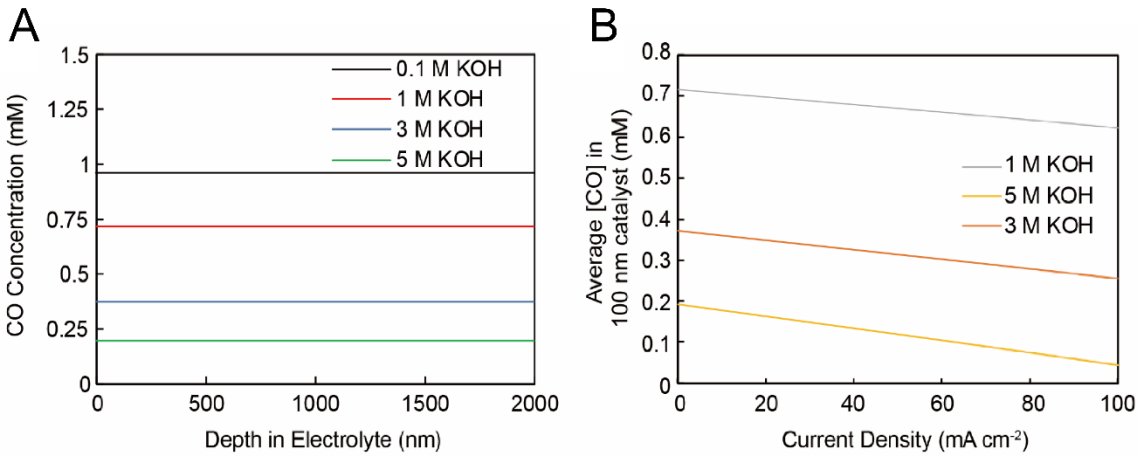


Figure S15. CO diffusion modelling. (A) CO concentrations at various depths in different KOH concentrations. The current density is 0 mA cm^{-2}. **(B)** CO concentrations in different KOH concentrations at various applied current densities.

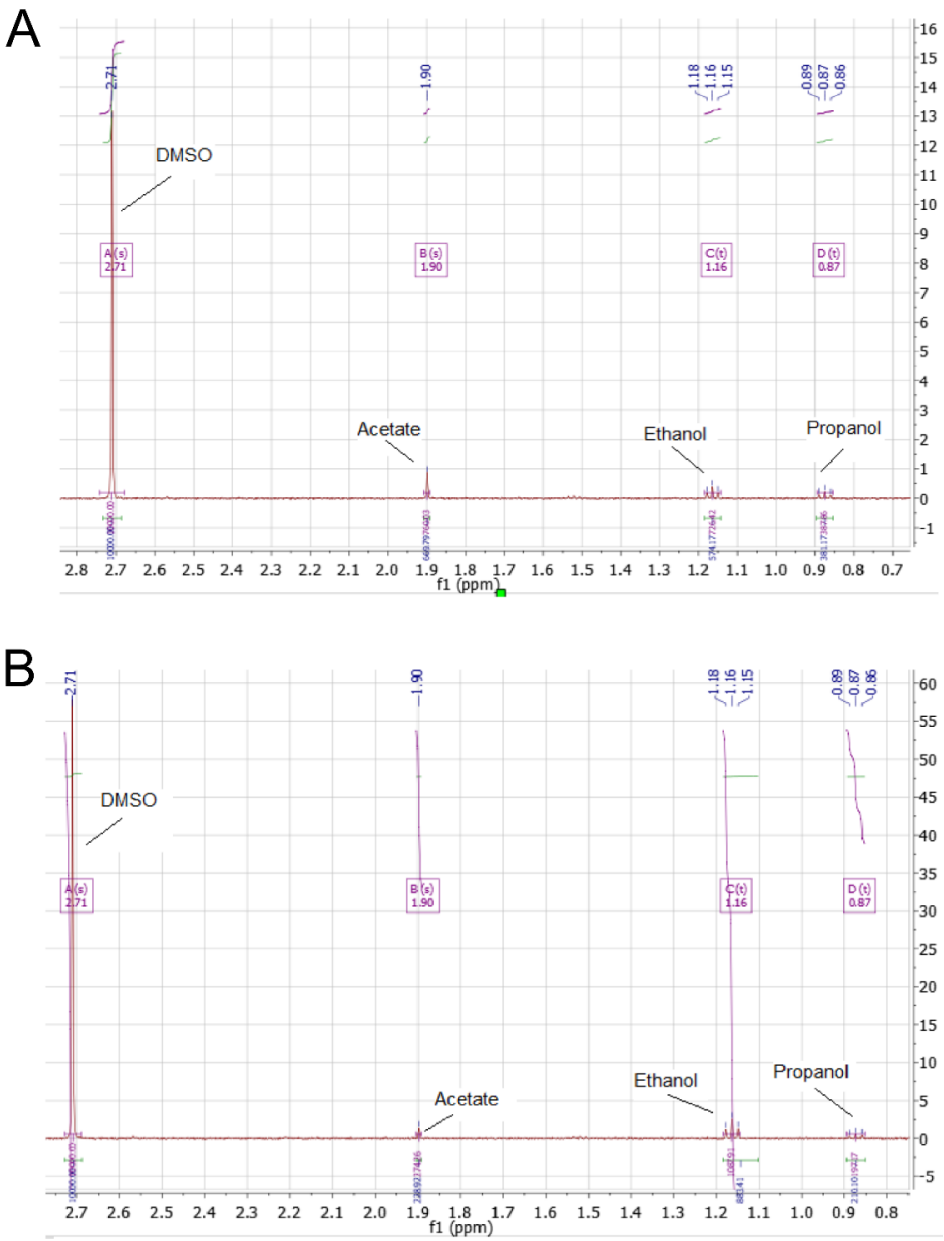


Figure S16. Representative of ^{1}H NMR spectra of the CORR liquid products at 160 mA cm^{-2}. (A) A representative of the CORR liquid products (acetate, ethanol and propanol) collected from the anodic liquid stream (the CORR products crossed over to the anodic stream through the AEM). **(B)** A representative of the CORR liquid products collected from the cathodic liquid stream (acetate, ethanol and propanol).

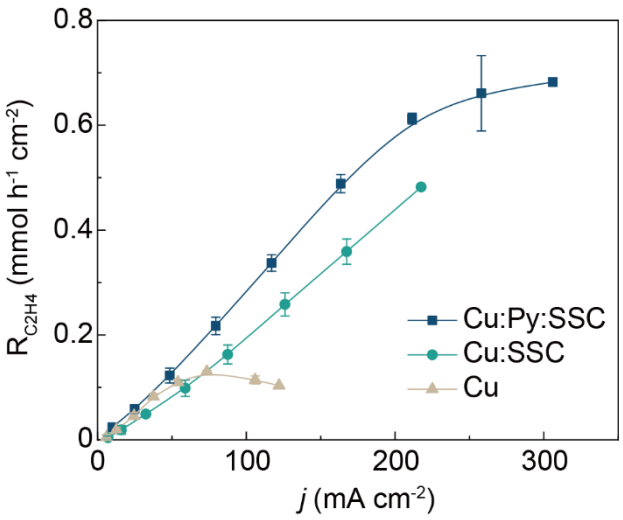


Figure S17. Comparison of C_2H_4 production rates obtained using different cathodes in MEAs with 3 M KOH. Error bars correspond to the standard deviation of 3 independent measurements.

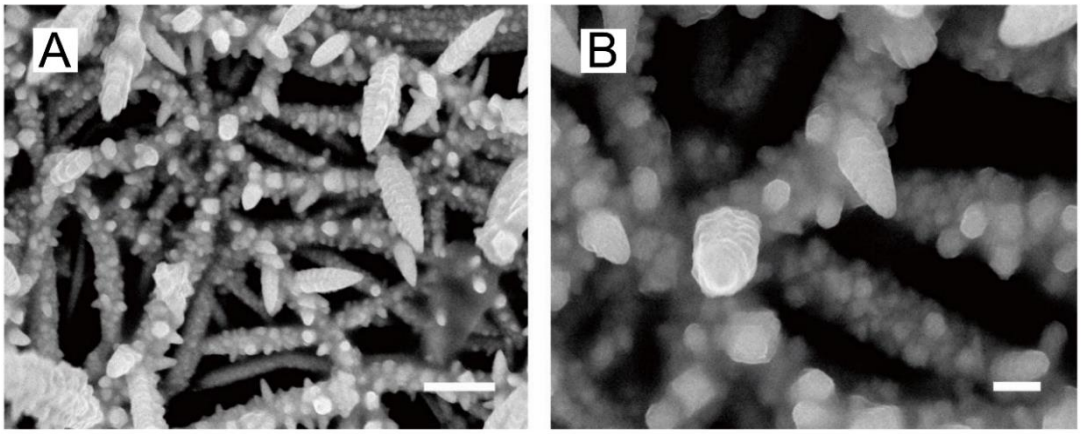


Figure S18. The SEM images of the Cu:Py:SSC cathode after 110-hour CORR operation. The scale bars are 1 μm and 200 nm in **(A)** and **(B)**.

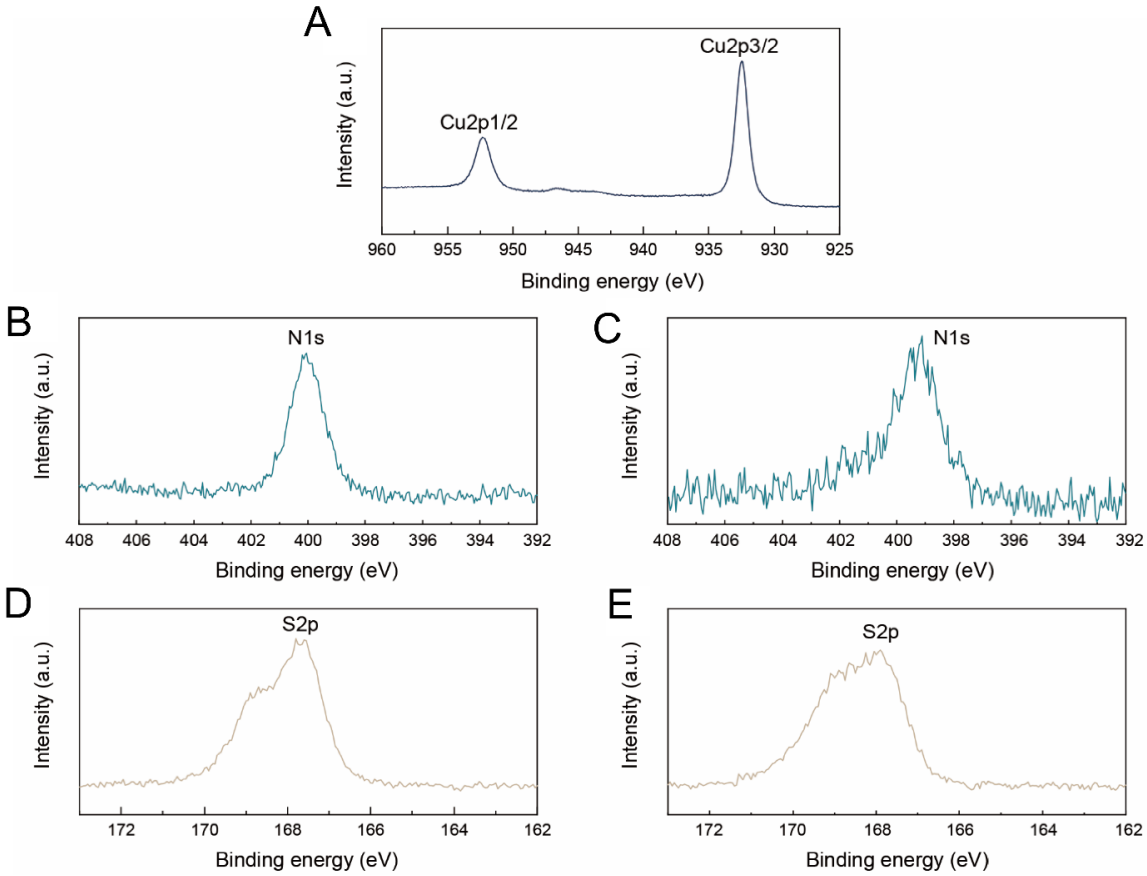


Figure S19. XPS analyses. (A) The Cu2p XPS of the as-made Cu:Py:SSC cathode. **(B-E)** The N1s and S2p XPS of the as-made Cu:Py:SSC cathode **(B, D)** and the same electrode after 110-hour CORR operation **(C, E)**. The N1s and S2p peaks in **(B, D)** indicate the existence of Py molecule and SSC ionomer on the Cu surface. After 110-hour of CORR operation, the Py molecule and SSC ionomer were still clearly seen as identified by the N1s and S2p peaks in **(C, E)**.

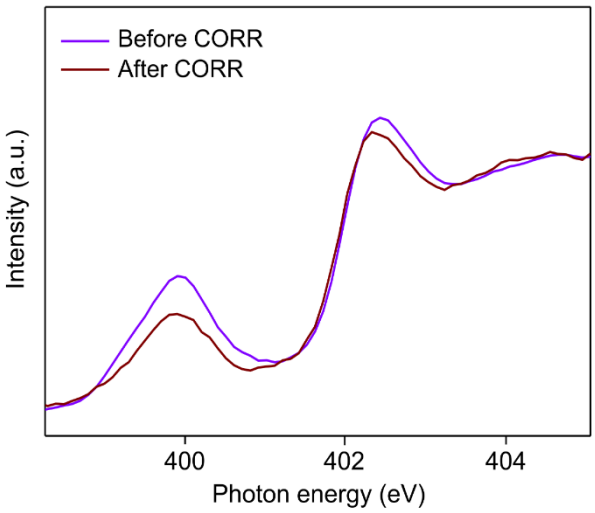


Figure S20. N K-edge sXAS spectra obtained on Cu:Py:SSC electrodes prior to and upon completion of 110-hour of CORR. The asymmetric N-C bonding with surrounding carbon splits the π* orbitals into two peaks centered at 400 and 402.5 eV,[12] respectively. A similar N valence orbital was confirmed from the electrode analyzed upon completion of 110-hour of electrosynthesis, indicating that the Py molecule was stable under reduction conditions.

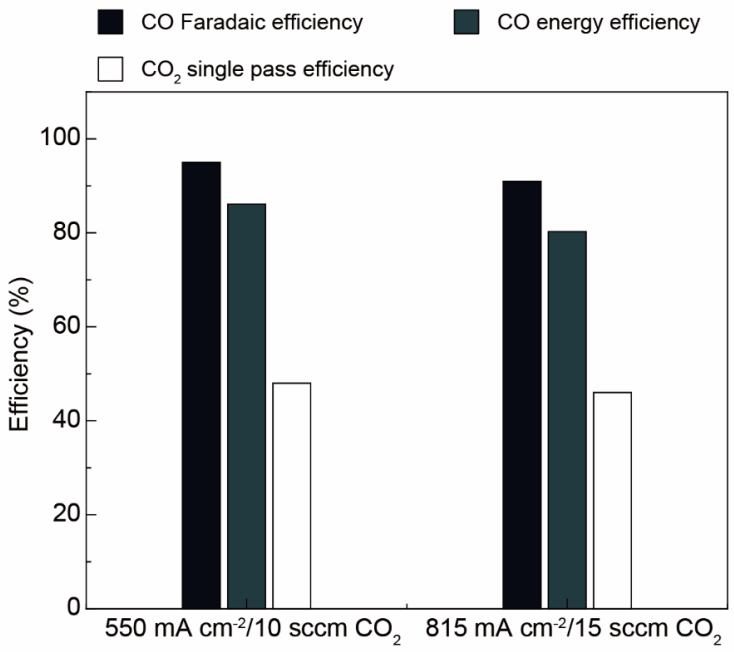


Figure S21. Comparison of CO_2-to-CO conversion at different current densities and CO_2 flow rates. To match an inlet CO flow rate of 4-5 sccm for high C_2H_4 concentration at the outlet of the MEA, the inlet CO_2 flow rate was set at 10 sccm. The current density for operating the SOEC was accordingly reduced to 550 mA cm^{-2} according the optimal current density:CO_2 flow rate ratio of 815:15 (mA cm^{-2} vs. sccm) for high CO_2-to-CO single-pass conversion. The operating temperature is 800 °C.

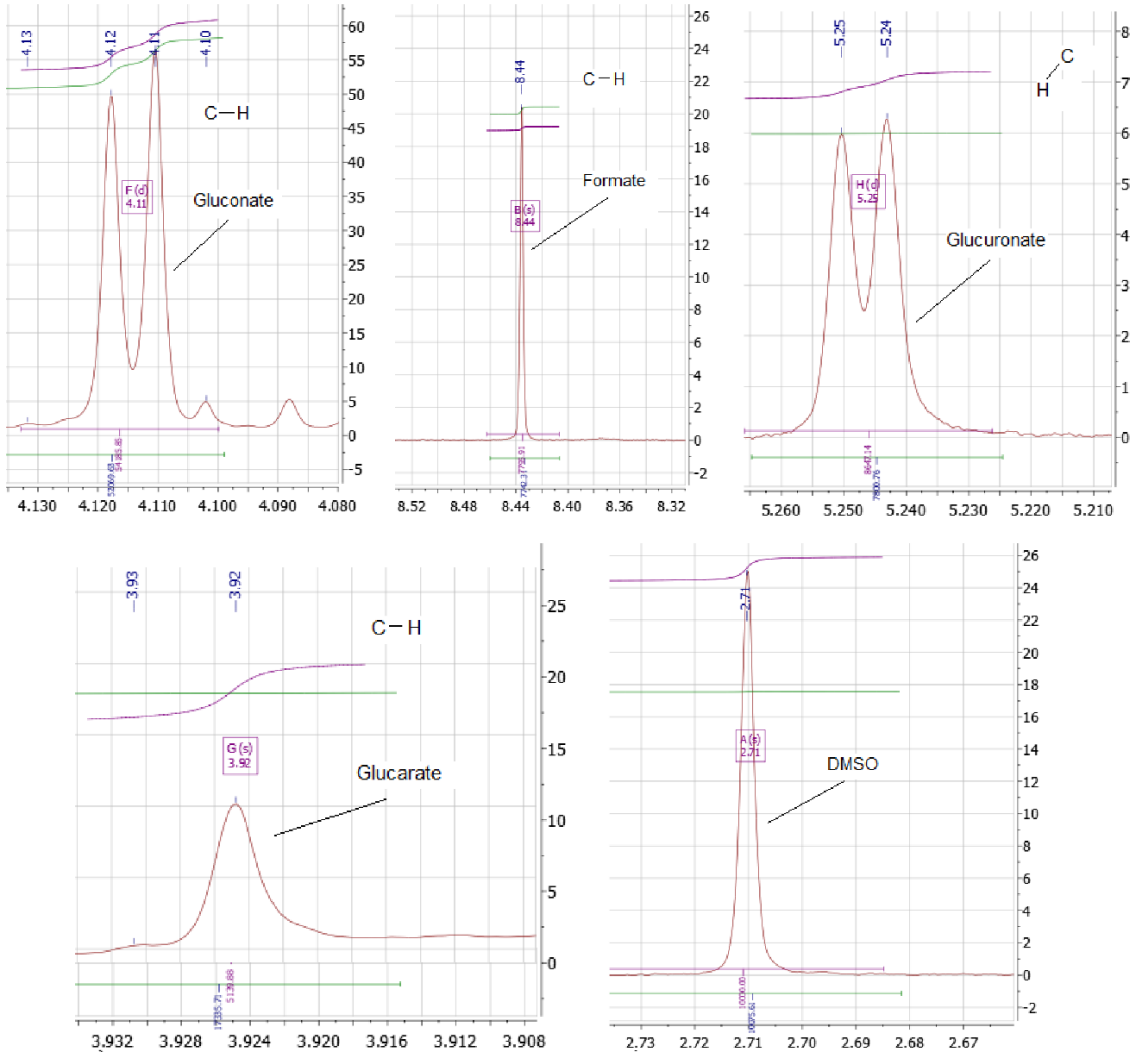


Figure S22. Representative of ^{1}H NMR spectra of the glucose electrooxidation reduction (GOR) products at 120 mA cm^{-2}.

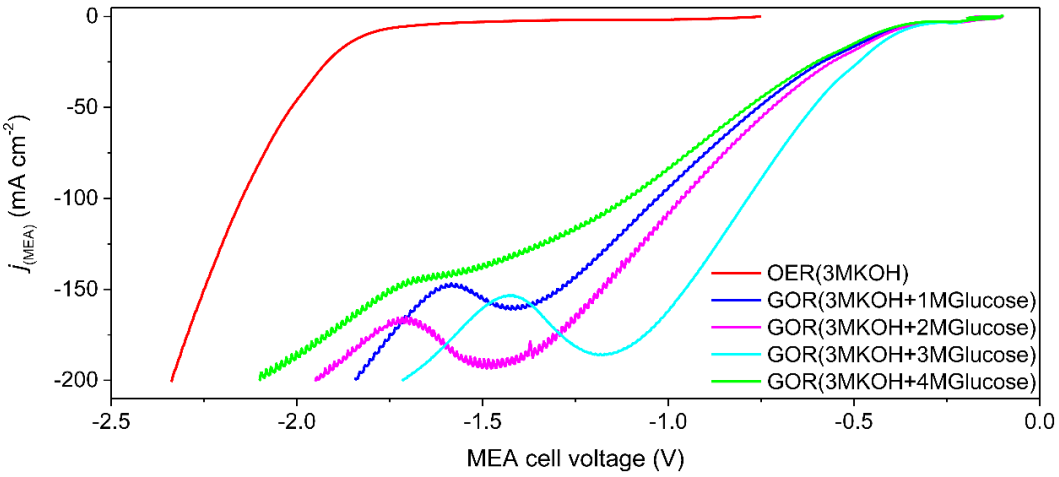


Figure S23. Linear sweep voltammetry curves of the MEAs using either oxygen evaluation reaction (OER) or glucose electrooxidation reaction (GOR) as the coupling reaction to CORR in the MEA of the cascade SOEC-MEA system. MEA operating conditions: anolyte flow rate: 20 mL/min; flow rate of CO (SOEC downstream): ~6 sccm; and cell temperature: 25 °C.

Table S1. Techno-economic assessment. Cost of C_2H_4 produced from CO_2 in different systems in base cases.

Parameters	CO_2RR MEA base case	CO_2RR flow cell base case	SOEC base case	CORR MEA base case
Input/Product	CO_2/C2H4	CO_2/C_2H_4	CO_2/CO	CO/C_2H_4
Product production rate	1	1	1	1
Cathode input cost ($/tonne)	30	30	30	404.77
Anode input cost ($/tonne)	5	5	5	5
Electricity cost (c kWh^{-1})	3	3	3	3
Electrolyser cost ($ kW^{-1})	300	300	250	300
Balance of plant (%)	50	50	50	50
Lang factor	1	1	1	1
Capacity factor	0.9	0.9	0.9	0.9
Cell voltage (V)	3.7	2.5	1.3	2.5
Faradaic efficiency (%)	60	60	100	60
Current density (mA cm^{-2})	150	150	800	150
Single pass conversion (%)	15	2.86	40	18
CO_2 crossover factor	3	20	0	0
Electrolyte Molarity (mol/L)	0.1	3	N/A	3
Electrolyte Cost ($/tonne)	750	1000	N/A	1000
System lifetime (year)	30	30	30	30
Catalyst/membrane lifetime (year)	5	5	5	5
Electrolyte lifetime (year)	1	1	N/A	1
Discount Rate (%)	5	5	5	5
Operation Temperature (°C)	25	25	800	25
Electrolyser specific cost distribution ($ (tonne product)$^{-1}$)				
Electrolyser capital	1238.76	837.00	4.53	558.00
Electrolyser operating	2453.16	1722.34	129.27	1888.48
Electrolyser installation	825.84	558.00	3.02	372.00
Cathode Separation	394.01	394.01	200.28	659.89
Anode Separation (Carbonate)	509.79	0.00	0.00	0.00
Carbonate Regeneration	0.00	2317.54	0.00	0.00
Heating (SOEC)	0.00	0.00	67.66	0.00
Overall cost	**5421.55**	**5828.89**	**404.77**	**3478.37**
Electrolyser specific energy distribution (GJ (tonne product)$^{-1}$)				
Electrolyser electricity	255.00	172.29	8.96	114.86
Cathode separation	4.98	4.98	1.97	10.05
Anode separation (Carbonate)	7.08	0.00	0.00	0.00
Carbonate regeneration	0.00	278.11	0.00	0.00
Heating (SOEC)	0.00	0.00	2.57	0.00
Overall energy	**267.05**	**455.38**	**13.49**	**124.91**

Table S2. Techno-economic assessment – Full breakdown of costs in base cases, with capital costs highlighted in grey.

	Electrolyser specific cost distribution ($ (tonne product)$^{-1}$)			
	CO_2RR MEA base case	**CO_2RR flow cell base case**	**SOEC base case**	**CORR MEA base case**
Electrolyser Capital	701.33	473.87	2.57	315.91
Electrolyser BoP	350.67	236.94	1.29	157.96
Electrolyser Installation	701.33	473.87	2.57	315.91
Catalyst & Membrane Capital	124.51	84.13	0.46	56.09
Catalyst & Membrane BoP	62.26	42.07	0.23	28.05
Catalyst & Membrane	124.51	84.13	0.46	56.09
Electrolyte	2.12	29.41	0.00	19.60
Cathode Input	94.29	94.29	47.14	809.54
Anode Input	19.29	19.29	0.00	6.43
Electricity	2124.97	1435.79	74.66	957.19
Other Operating Costs	212.50	143.58	7.47	95.72
Cathode Separation Operating	41.49	41.49	16.38	83.71
Cathode Separation Capital	141.01	141.01	73.56	230.47
Cathode Separation BoP	70.50	70.50	36.78	115.24
Cathode Separation Installation	141.01	141.01	73.56	230.47
Anode Separation Operating	58.96	0.00	0.00	0.00
Anode Separation Capital	180.33	0.00	0.00	0.00
Anode Separation BoP	90.17	0.00	0.00	0.00
Anode Separation Installation	180.33	0.00	0.00	0.00
Carbonate Regeneration	0.00	2317.54	0.00	0.00
Heating	0.00	0.00	67.66	0.00
Overall cost	**5421.55**	**5828.89**	**404.77**	**3478.37**

Note 1: BoP = Balance of Plant

Note 2: All values in the SOEC column are USD per tonne of CO produced. Thus, it is needed to multiply these by 2 in order to find USD per tonne of C_2H_4.

Note 3: All 3 columns assume a production rate of 1 tonne product/day. This means that the 1st and 3rd columns report numbers for a plant producing 1 tonne C_2H_4 per day. Column 2 reports numbers for a plant producing 1 tonne CO per day.

Note 4: The cathode input costs for the CORR step are simply 2 times the final cost of CO for the SOEC step since 2 tonnes CO are required to produced 1 tonne C_2H_4 with no loss.

Considering only capital cost distributions in Table S1B (grey rows), the total capital costs of the direct and cascade approaches can be compared as follows:

Total capital cost estimate for direct route electrode (CO_2RR MEA) = 1720.78 USD/tonne C_2H_4

Capital cost estimate for alkaline CORR MEA = 903.72 USD/tonne C_2H_4

Added capital cost for the SOEC step to provide CO reactant for the alkaline MEA = 114.89 USD/tonne CO corresponds to 2 x 114.89 USD/tonne C_2H_4 = 229.78 USD/tonne C_2H_4

Total capital cost for cascade route = 1133.50 USD/tonne C_2H_4

Table S3. Techno-economic assessment. Cost of C_2H_4 produced from CO_2 in different systems in ideal cases.

Parameters	CO_2RR MEA ideal case	CO_2RR flow cell ideal case	SOEC ideal case	CORR MEA ideal case
Input/Product	CO_2/C_2H_4	CO_2/C_2H_4	CO_2/CO	CO/C_2H_4
Product production rate	1	1	1	1
Cathode input cost ($/tonne)	30	30	30	292.25
Anode input cost ($/tonne)	5	5	5	5
Electricity cost (c kWh^{-1})	3	3	3	3
Electrolyser cost ($ kW^{-1})	300	300	250	300
Balance of plant (%)	50	50	50	50
Lang factor	1	1	1	1
Capacity factor	0.9	0.9	0.9	0.9
Cell voltage (V)	3.7	2.5	1.3	2.5
Faradaic efficiency (%)	95	95	100	95
Current density (mA cm^{-2})	200	200	800	200
Single pass conversion (%)	23.75	4.52	90	28.5
CO_2 crossover factor	3	20	0	0
Electrolyte Molarity (mol/L)	0.1	3	N/A	3
Electrolyte Cost ($/tonne)	750	1000	N/A	1000
System lifetime (year)	30	30	30	30
Catalyst/membrane lifetime (year)	5	5	5	5
Electrolyte lifetime (year)	1	1	N/A	1
Discount Rate (%)	5	5	5	5
Operation Temperature (°C)	25	25	800	25
Electrolyser specific cost distribution ($ (tonne product)$^{-1}$)				
Electrolyser capital	586.78	396.47	4.53	264.32
Electrolyser operating	1590.87	1125.00	129.27	1265.21
Electrolyser installation	391.19	264.32	3.02	176.21
Cathode Separation	133.15	133.15	111.53	389.21
Anode Separation (Carbonate)	509.79	0.00	0.00	0.00
Carbonate Regeneration	0.00	2317.54	0.00	0.00
Heating (SOEC)	0.00	0.00	43.89	0.00
Overall cost	**3211.78**	**4236.48**	**292.25**	**2094.95**
Electrolyser specific energy distribution (GJ (tonne product)$^{-1}$)				
Electrolyser electricity	161.05	108.82	8.96	72.55
Cathode separation	1.12	1.12	0.87	4.90
Anode separation (Carbonate)	7.08	0.00	0.00	0.00
Carbonate regeneration	0.00	278.11	0.00	0.00
Heating (SOEC)	0.00	0.00	1.14	0.00
Overall energy	**169.24**	**388.04**	**10.97**	**77.44**

Table S4. The CORR-to-C_2H_4 performance of bare Cu catalyst. Error bars correspond to the standard deviation of 3 independent measurements.

Full cell potential (V)	*j* (mA cm^{-2})	Faradaic efficiency (%)			j_{C2H4} (mA cm^{-2})	Energy efficiency (%)
		H_2	CH_4	C_2H_4		
-2.0	9±3	8	1	23±5	2±1	13±3
-2.1	19±5	13±2	0.3±0.1	35±1	7±2	18±1
-2.2	31±6	17±1	0.2	44	14±3	22
-2.3	45±7	23±1	0.1	47±3	22±2	21±2
-2.4	65±9	30±3	0.2±0.1	41±3	26±2	18±1
-2.5	96±22	38±5	0.5±0.3	29±9	26±2	13±4
-2.6	98	43	0.3	27	26	11
-2.7	122	54	0.5	18	22	7

Operating conditions: anolyte: 3 M KOH; anolyte flow rate: 20 mL/min; CO flow rate: 80 sccm; and cell temperature: 25 °C.

Table S5. The CORR-to-C_2H_4 performance of the Cu:SSC catalyst. Error bars correspond to the standard deviation of 3 independent measurements.

Full cell potential (V)	*j* (mA cm^{-2})	Faradaic efficiency (%)			j_{C2H4} (mA cm^{-2})	Energy efficiency (%)
		H_2	CH_4	C_2H_4		
-2.0	12±5	27±3	0.4±0.1	15±2	2±1	8±1
-2.1	25±9	22±6	0.2±0.1	25±5	7±4	13±2
-2.2	44±13	18±5	0.2±0.1	32±4	14±6	16±2
-2.3	71±9	15±3	0.1	36	26±4	17±1
-2.4	105±11	12±2	0.1	41±1	42±4	18±1
-2.5	146±11	11±1	0.1	44	64±5	19±1
-2.6	193±15	10±1	0.1	46	89±7	19±1
-2.7	246±20	9±1	0.2	48	117±9	19±1
-2.8	300±22	11±1	0.3	47±5	139±4	18±2
-2.9	367±20	15±3	0.4±0.1	39±6	142±13	14±2
-3.0	438±28	22±3	1	25±7	108±24	9±2
-3.1	468	28	1.8	20.7	97	7

Operating conditions: anolyte: 3 M KOH; anolyte flow rate: 20 mL/min; CO flow rate: 80 sccm; and cell temperature: 25 °C.

Table S6. The CORR-to-C_2H_4 performance of the Cu:Py:SSC catalyst. Error bars correspond to the standard deviation of 3 independent measurements.

Full cell potential (V)	j (mA cm^{-2})	Faradaic efficiency (%)			j_{C2H4} (mA cm^{-2})	Energy efficiency (%)
		H_2	CH_4	C_2H_4		
-2.0	10±1	33±3	1	48±3	5±1	26±2
-2.1	25±1	31±4	0.3	52±3	13±1	26±1
-2.2	49±2	26±3	0.2	57±1	29±1	28±1
-2.3	80±3	21±2	0.1	61±1	48±2	29±1
-2.4	117±2	17±2	0.2	63±1	74±2	28±1
-2.5	164±3	14±2	0.3	65±1	106±3	28±1
-2.6	212±5	17±2	1	61±1	129±1	25±1
-2.7	258±4	27±5	2±1	48	124±3	19
-2.8	312±6	39±10	3±1	32±4	99±14	12±1

Operating conditions: anolyte: 3 M KOH; anolyte flow rate: 20 mL/min; CO flow rate: 80 sccm; and cell temperature: 25 °C.

Table S7. The CORR-to-C_2H_4 performance of the Cu:Py:SSC catalyst using 0.1 M KOH anolyte. Error bars correspond to the standard deviation of 3 independent measurements.

Full cell potential (V)	j (mA cm^{-2})	Faradaic efficiency (%)			j_{C2H4} (mA cm^{-2})	Energy efficiency (%)
		H_2	CH_4	C_2H_4		
-2.2	9±1	63±4	1	23±2	2±1	11±1
-2.4	26±1	42±3	0.3±0.1	34±1	9±1	15±1
-2.6	56±2	32±2	0.6±0.1	42±1	23±1	17±1
-2.8	104±2	27±2	1	47±2	48±1	18±1
-3.0	163±3	25±4	2±1	44±1	72±1	16±1
-3.2	235±5	30±4	3±1	38±1	90±1	13±1
-3.4	287±5	36±4	4±1	31±1	89±2	10
-3.6	416±16	44±7	4±1	21±1	92±6	6

Operating conditions: anolyte flow rate: 20 mL/min; CO flow rate: 80 sccm; and cell temperature: 25 °C.

Table S8. The CORR-to-C_2H_4 performance of the Cu:Py:SSC catalyst using 1 M KOH anolyte. Error bars correspond to the standard deviation of 3 independent measurements.

Full cell potential (V)	j (mA cm^{-2})	Faradaic efficiency (%)			j_{C2H4} (mA cm^{-2})	Energy efficiency (%)
		H_2	CH_4	C_2H_4		
-2.2	29±1	42±3	0.3	38±1	11±1	18
-2.3	43±1	38±4	0.2	42±1	18±1	19±1
-2.4	69±2	30±3	0.2	48±1	33±2	21±1
-2.5	108±2	23±2	0.4	50±2	54±3	21±1
-2.6	155±3	20±2	1	52±2	81±4	21±1
-2.7	206±4	20±2	1	51±2	105±5	20±1
-2.8	262±6	22±2	1	48±2	127±7	18±1
-2.9	329±7	28±2	2±1	41±1	134±6	15
-3.0	398±6	35±5	3±1	32±1	126±7	11±1

Operating conditions: anolyte flow rate: 20 mL/min; CO flow rate: 80 sccm; and temperature: 25 °C.

Table S9. The CORR-to-C_2H_4 performance of the Cu:Py:SSC catalyst using 5 M KOH anolyte. Error bars correspond to the standard deviation of 3 independent measurements.

Full cell potential (V)	j (mA cm^{-2})	Faradaic efficiency (%)			j_{C2H4} (mA cm^{-2})	Energy efficiency (%)
		H_2	CH_4	C_2H_4		
-1.9	9±1	25±2	0.7	44±1	4	25±1
-2.0	21±1	21±3	0.3	53±1	11±1	28±1
-2.1	42±3	18±3	0.2	58±1	24±2	29±1
-2.2	66±4	17±3	0.2	61±1	40±2	29±1
-2.3	96±2	14±3	0.1	64±1	62±1	30±1
-2.4	135±3	20±5	0.2	58±1	78±1	26±1
-2.5	174±4	29±4	0.4	47±2	81±1	20±1
-2.6	218±4	45±7	2	31±1	68±1	14±1

Operating conditions: anolyte flow rate: 20 mL/min; CO flow rate: 80 sccm; temperature: 25 °C.

Table S10. The CORR product distribution of the Cu:Py:SSC catalyst.

Full cell potential (V)	*j* (mA cm^{-2})	Faradaic efficiency (%)						
		H_2	CH_4	C_2H_4	EtOH	Acetate	Propanol	Total
-2.1	25	32.2	0.4	53.9	4.4	6.3	4.5	101.7
-2.3	80	21.4	0.1	62.9	6.3	8.4	2.1	101.2
-2.5	160	13.6	0.3	66.2	5.7	10.9	1.8	98.5
-2.7	250	28.9	1.9	49.3	4.9	11.9	1.7	98.6

Operating conditions: anolyte: 3 M KOH; anolyte flow rate: 20 mL/min; flow rate: 80 sccm; and cell temperature: 25 °C.

Table S11. The CORR-to-C_2H_4 performance of the Cu:Py:SSC catalyst at 100 mA cm^{-2} under various CO partial pressures. Error bars correspond to the standard deviation of 3 independent measurements.

$P_{CO}/(P_{N2}+P_{CO})$ (%)	Full cell potential (V)	Faradaic efficiency (%)			j_{C2H4} (mA cm^{-2})	Energy efficiency (%)
		H_2	CH_4	C_2H_4		
100	-2.32	14±1	0.1	60±2	60±2	27.5±1
80	-2.33	15±2	0.1	61±2	61±2	27.5±0.5
60	-2.34	16±2	0.1	62±2	62±2	27.5±0.5
40	-2.35	16±2	0.2	63±2	64±2	28.5±1
30	-2.36	16±2	0.2	65±2	66±2	30±1
20	-2.37	19±2	0.3	61±3	62±3	28±1
10	-2.38	23±3	0.3	57±3	57±3	25.5±1

Operating conditions: anolyte: 3 M KOH; anolyte flow rate: 20 mL/min; flow rate ($CO+N_2$): 80 sccm; and cell temperature: 25 °C.

Table S12. A summary of C_2H_4 production at various CO flow rates. The Cu:Py:SSC was tested at 160 mA cm^{-2} and bare Cu was tested at 40 mA cm^{-2}, respectively, to ensure the highest C_2H_4 FE was achieved for each sample during the test.

Cu:Py:SSC (at 160 mA cm^{-2})			Bare Cu (at 40 mA cm^{-2})		
CO flow rate (s.c.c.m.)	**C_2H_4 FE (%)**	**C_2H_4 concentration (%)**	**CO flow rate (s.c.c.m.)**	**C_2H_4 FE (%)**	**C_2H_4 concentration (%)**
86	62 ± 1	1.1	84	46 ± 5	0.2
75	62 ± 1	1.3	73	48 ± 6	0.3
66	61 ± 1	1.5	63	47 ± 4	0.3
57	61 ± 2	1.7	53	47 ± 4	0.4
46	60 ± 3	2.1	43	44 ± 3	0.4
36	59 ± 5	2.7	34	42 ± 2	0.5
27	58 ± 5	3.8	25	40 ± 3	0.8
16	54 ± 6	7.2 ± 1	16	33 ± 1	1.6
13	48 ± 4	9.2 ± 2	11	30 ± 1	1.9
10	43 ± 8	12.6 ± 3	9	32 ± 1	2.4
7	43 ± 1	19.4	6	28 ± 7	3.7 ± 1
4	41 ± 1	35.7	2	26 ± 1	8.0

Operating conditions: anolyte flow rate: 20 mL/min; temperature: 25°C.

Table S13. A summary of CO_2-to-C_2H_4 production using different systems and catalysts. The performance of C_2H_4 production in both the cascade SOEC-MEA system and single CORR MEA electrolyser.

System	$CO_{(2)}$-to-C_2H_4 Faradaic efficiency (%)	$CO_{(2)}$-to-C_2H_4 energy efficiency (%)	$CO_{(2)}$-to-C_2H_4 single-pass efficiency (%)	C_2H_4 concentration in gas-product stream (%)	Operating duration and corresponding C_2H_4 partial current density	Reference
Cascade SOEC-MEA system	N.A.	20	11	25	N.A.	This work
CORR MEA using metal:molecule:ionomer catalysts	65 (in a single MEA electrolyser) 54 (in the cascade SOEC-MEA system)	28 (in a single MEA electrolyser) 24 (in the cascade SOEC-MEA system)	26	36	110 h/92 mA cm^{-2}	This work
CO_2RR MEA using 300 nm Cu/PTFE	48	14	8	30	100 h/55 mA cm^{-2} 24 h/100 mA cm^{-2}	Ref. 11
Pressurized CORR MEA	35	16	12	13	24 h/57 mA cm^{-2}	Ref. 8
CO_2RR flow cell having an abrupt interface	70	34	0.15	0.15	150 h/70 mA cm^{-2}	Ref. 5
CO_2RR MEA using Cu:pyridinium	64	20	1	1	190 h/72 mA cm^{-2}	Ref. 6
CO_2RR MEA	15	9	N. R.	N. R.	N. R./0.6 mA cm^{-2}	Ref. 34
CO_2RR micro flow cell	91	20	~0.4	~0.4	0.7 h/7 mA cm^{-2}	Ref. 35

N.R. indicates that the data was not reported in the corresponding reference.

Table S14. The CORR product distribution of the Cu:Py:SSC catalyst in the MEA of the cascade SOEC-MEA system.

Full cell potential (V)	*j* (mA cm^{-2})	Faradaic efficiency (%)						
		H_2	CH_4	C_2H_4	EtOH	Acetate	Propanol	Total
-2.13	25	36.6	1.1	48.6	3.9	5.6	3.7	99.3
-2.33	80	27.9	0.9	53.4	5.3	7.8	1.9	97.1
-2.41	120	21.3	0.8	58.7	5.6	10.1	1.7	98.2
-2.51	160	29.7	2.4	46.6	4.1	10.3	1.5	94.6
-2.62	200	37.1	2.9	41.4	3.6	9.1	1.3	95.4

Operating conditions: anolyte: 3 M KOH; anolyte flow rate: 20 mL/min; flow rate of CO (SOEC downstream): ~6 sccm; and cell temperature: 25 °C.

Table S15. The glucose oxidation reaction (GOR) product distribution of the Pt-C catalyst in the MEA of the cascade SOEC-MEA system using glucose oxidation as the anodic reaction.

Full cell potential (V)	*j* (mA cm^{-2})	Faradaic efficiency (%)					$J_{gluconate}$ (mA cm^{-2})
		Gluconate	Formate	Glucarate	Glucuronate	Total	
-0.77	40	36.4	7.4	27.6	30.2	101.6	14.6
-1.08	80	53.6	5.6	22.1	21.1	102.4	42.9
-1.27	120	59.1	6.2	17.3	16.8	99.4	70.9
-1.43	160	66.5	6.1	15.4	13.1	101.1	106.4
-1.63	200	61.8	5.1	10.7	8.7	86.3	123.6

MEA operating conditions: anolyte: 3 M KOH+3 M Glucose; anolyte flow rate: 20 mL/min; flow rate of CO (SOEC downstream): ~6 sccm; and cell temperature: 25 °C.

Table S16. The CORR-to-C_2H_4 performance of the Cu:Py:SSC catalyst in the MEA of the cascade SOEC-MEA system using glucose oxidation as the anodic reaction. Error bars correspond to the standard deviation of 3 independent measurements.

Full cell potential (V)	j (mA cm^{-2})	Faradaic efficiency (%)			j_{C2H4} (mA cm^{-2})
		H_2	CH_4	C_2H_4	
-0.97	20	16±2	0.1	35±2	7±1
-1.18	40	14±2	0.1	43±2	17±1
-1.32	60	13±2	0.1	47±2	28±1
-2.28	80	12±2	0.1	50±2	40±2
-2.56	100	11±1	0.1	54±2	54±2
-2.71	120	10±1	0.1	56±2	67±3
-2.83	140	9±1	0.1	58±1	82±2
-3.03	160	11±2	0.1	53±2	85±3
-3.11	180	13±3	0.1	47±3	85±5
-3.22	200	15±3	0.1	43±3	86±6

MEA operating conditions: anolyte: 3 M KOH+1 M Glucose; anolyte flow rate: 20 mL/min; flow rate of CO (SOEC downstream): ~6 sccm; and cell temperature: 25 °C.

Table S17. The CORR-to-C_2H_4 performance of the Cu:Py:SSC catalyst in the MEA of the cascade SOEC-MEA system using glucose oxidation as the anodic reaction. Error bars correspond to the standard deviation of 3 independent measurements.

Full cell potential (V)	j (mA cm^{-2})	Faradaic efficiency (%)			j_{C2H4} (mA cm^{-2})
		H_2	CH_4	C_2H_4	
-0.68	20	15±2	0.1	39±2	7±1
-0.96	40	14±2	0.1	17±1	17±1
-1.15	60	13±2	0.1	47±2	28±1
-1.29	80	12±2	0.1	50±2	40±2
-1.38	100	11±1	0.1	54±1	54±1
-1.49	120	11±1	0.1	55±2	66±2
-1.61	140	11±1	0.1	57±1	80±2
-2.56	160	12±1	0.1	53±2	85±3
-2.62	180	14±2	0.1	49±2	88±4
-2.71	200	16±2	0.1	45±2	90±4

MEA operating conditions: anolyte: 3 M KOH+2 M Glucose; anolyte flow rate: 20 mL/min; flow rate of CO (SOEC downstream): ~6 sccm; and cell temperature: 25 °C.

Table S18. The CORR-to-C_2H_4 performance of the Cu:Py:SSC catalyst in the MEA of the cascade SOEC-MEA system using glucose oxidation as the anodic reaction. Error bars correspond to the standard deviation of 3 independent measurements.

Full cell potential (V)	j (mA cm^{-2})	Faradaic efficiency (%)			j_{C2H4} (mA cm^{-2})
		H_2	CH_4	C_2H_4	
-0.54	20	13±2	0.1	36±2	7±1
-0.77	40	12±2	0.1	41±2	17±1
-0.96	60	12±2	0.1	46±2	28±1
-1.08	80	11±2	0.1	49±2	40±2
-1.19	100	10±1	0.1	52±2	52±2
-1.27	120	10±1	0.1	55±2	66±2
-1.35	140	10±1	0.1	57±1	80±2
-1.43	160	12±1	0.1	54±2	87±3
-1.52	180	13±2	0.1	52±2	94±4
-1.63	200	16±2	0.1	44±2	88±4

MEA operating conditions: anolyte: 3 M KOH+3 M Glucose; anolyte flow rate: 20 mL/min; flow rate of CO (SOEC downstream): ~6 sccm; and cell temperature: 25 °C.

Table S19. The CORR-to-C_2H_4 performance of the Cu:Py:SSC catalyst in the MEA of the cascade SOEC-MEA system using glucose oxidation as the anodic reaction. Error bars correspond to the standard deviation of 3 independent measurements.

Full cell potential (V)	j (mA cm^{-2})	Faradaic efficiency (%)			j_{C2H4} (mA cm^{-2})
		H_2	CH_4	C_2H_4	
-0.59	20	11±1	0.1	34±2	6±1
-0.77	40	10±1	0.1	39±2	16±1
-1.09	60	10±1	0.1	43±2	26±1
-1.35	80	9±1	0.1	44±2	35±2
-1.46	100	9±1	0.1	47±2	47±2
-1.59	120	10±1	0.1	50±2	60±2
-1.68	140	12±2	0.1	52±1	73±2
-1.79	160	15±2	0.1	48±2	77±3
-1.87	180	18±2	0.1	44±2	79±3
-1.94	200	20±3	0.1	40±3	80±6

MEA operating conditions: anolyte: 3 M KOH+4 M Glucose; anolyte flow rate: 20 mL/min; flow rate of CO (SOEC downstream): ~6 sccm; and cell temperature: 25 °C.

Table S20. The CORR product distribution of the Cu:Py:SSC catalyst in the MEA of the cascade SOEC-MEA system using glucose oxidation as the anodic reaction.

Full cell potential (V)	*j* (mA cm^{-2})	Faradaic efficiency (%)						
		H_2	CH_4	C_2H_4	EtOH	Acetate	Propanol	Total
-0.77	40	12.9	0.1	45.1	11.3	14.4	11.6	95.4
-1.08	80	10.3	0.1	51.6	15.0	15.2	9.1	101.3
-1.27	120	9.7	0.1	55.1	13.8	16.1	6.9	101.6
-1.43	160	12.1	0.1	53.8	11.2	19.1	4.8	101.1
-1.63	200	18.8	0.1	45.9	8.3	16.8	4.2	94.1

Operating conditions: anolyte: 3 M KOH+3 M Glucose; anolyte flow rate: 20 mL/min; flow rate of CO (SOEC downstream): ~6 sccm; and cell temperature: 25 °C.

Table S21. Summary of inputs for the TEA of the CORR:OER and CORR:GOR couples in the MEA of the cascade SOEC-MEA system.

Parameters	SOEC base case	CORR:OER MEA	CORR:GOR MEA	CO_2RR MEA	SOEC Optimistic	CORR Optimistic
Cathode input cost	30	404.77	404.77	30	30	247.81
Anode input cost	5	5	5	5	5	5
Electricity cost (c	3	3	3	3	2	2
Electrolyser cost ($	250	300	300	300	250	300
Balance of plant (%)	50	50	50	50	50	50
Lang factor	1	1	1	1	1	1
Capacity factor	0.9	0.9	0.9	0.9	0.9	0.9
Cell voltage (V)	1.3	2.41	1.27	3.7	1.3	1.7
Faradaic efficiency	100	58.7	55	60	100	95
Current density (mA	800	120	120	120	800	1000
Single pass	40	17.61	16.5	15	90	95
CO_2 crossover factor	0	0	0	3	0	0
Electrolyte Molarity	N/A	3	3	0.1	N/A	0.1
Electrolyte Cost	N/A	1000	1000	750	N/A	750
System lifetime (year)	30	30	30	30	30	30
Catalyst/membrane	5	5	5	5	5	5
Electrolyte lifetime	N/A	1	1	1	N/A	1
Discount Rate (%)	5	5	5	5	5	5
Operation	800	25	25	25	800	25
Electrolyser specific cost distribution ($ (tonne ethylene)$^{-1}$)						
Electrolyser capital	4.53	687.28	386.54	1238.76	4.53	35.95
Electrolyser operating	129.27	1878.50	1426.21	2453.16	101.89	805.38
Electrolyser	3.02	458.19	257.69	825.84	3.02	23.96
Cathode Separation	200.28	674.84	720.57	394.01	109.10	123.09
Anode Separation	0.00	0.00	0.00	509.79	0.00	0.00
Carbonate	0.00	0	0	0.00	0.00	0
Heating (SOEC)	67.66	0	0	0.00	29.26	0
Overall cost	**405**	**3699**	**2791**	**5422**	**248**	**988**
Electrolyser specific energy distribution (GJ (tonne ethylene)$^{-1}$)						
Electrolyser electricity	8.96	113.18	63.66	255.00	8.96	49.33
Cathode separation	1.97	10.35	11.32	4.98	0.87	1.03
Anode separation	0.00	0.00	0.00	7.08	0.00	0.00
Carbonate	0.00	0.00	0.00	0.00	0.00	0.00
Heating (SOEC)	2.57	0.00	0.00	0.00	1.14	0.00
Overall energy	**13.5**	**123.5**	**75**	**267.1**	**11.0**	**50.4**

Supplemental References Notes

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